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RAY T. BAYLESS, *Editor*

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APPLICATION OF THERMODYNAMICS TO THE DEOXIDATION OF LIQUID STEEL

By John Chipman

Abstract

The methods by which thermodynamics may be applied to the study of reactions in liquid steel are briefly reviewed. Experimental evidence is presented to show that the oxygen in liquid steel is present in the form of a dissolved oxide whose molecule contains one atom of oxygen. This oxide is considered to be FeO. The free energy and activity of this oxide in liquid steel are computed from the equilibrium data involving steam and hydrogen.

Additional evidence is presented to show that at low percentages carbon is present in austenite and in liquid iron mainly as Fe_3C. Thermodynamically calculated equilibrium constants involving this carbide, FeO, CO and CO_2, are in fair agreement with the experimental results of Vacher and Hamilton.

The free energies of a number of metals (dissolved in liquid steel) and of their oxides are obtained from various types of thermodynamic data and the results are used to compute the equilibrium constants in the reactions by which dissolved FeO is removed from the steel bath by the respective metals. From these equilibrium constants the deoxidizing powers of the alloys are computed. The metals under consideration are the following, arranged in order of increasing deoxidizing power at 1600 degrees Cent.: chromium, manganese, silicon, titanium, vanadium, zirconium, aluminum, magnesium, and calcium.

Introduction

IN the application of the principles of physical chemistry to the problems of steel making, we must recognize at least three main lines along which fundamental research can profitably be conducted. The first of these has to do with the physical properties of substances and of mixtures in slag and metal—their melting points, viscosities, thermal capacities, crystalline habits, surface tensions and

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colloidal behavior. The second is concerned with the equilibrium relationships and energy changes among the many physical and chemical processes which are constantly taking place in the steel bath, and with what has rather loosely been called the "affinity" of substances taking part in reactions. The third is the complex problem of the rates of chemical reactions in the bath, as, for instance, the rate of elimination of carbon and rates of diffusion of substances through the metal or of transfer between metal and slag.

In attacking any of the major practical problems connected with the melting and refining of steel, it is necessary to draw upon our knowledge of all three of these branches of physical chemistry. It is, however, only with the second of these broad fields of investigation that the present paper will be concerned. The science of chemical thermodynamics or "energetics" involves not only a study of the energy changes—the so-called driving forces—of chemical reactions, but, of greater practical usefulness, the equilibrium or limiting states towards which reactions progress. The importance of a thorough study of equilibrium under conditions of the steel bath arises in part from the fact that many chemical reactions actually attain a state of equilibrium during the making of a heat of steel. Even in the case of a reaction which on account of its slow rate does not actually reach equilibrium, a knowledge of the equilibrium state gives us definite information as to whether or not the reaction is possible and the limits which it will eventually attain.

The now classical paper of Henry Le Chatelier(1)* in 1912 marks the first serious attempt to apply thermodynamic methods to the problems of steel making. The subsequent papers of Styri(2), McCance(3), and H. Schenck(4) contributed in a qualitative way to our knowledge of equilibrium in the steel bath. Many of the equilibrium constants which they sought to calculate have been determined recently by direct experimental methods both in the laboratory and in open-hearth operation; and in general it may be remarked that when experimental results at actual steel making temperatures are available they are to be preferred to the results of extrapolations from lower temperatures. An excellent review of the literature on systems in equilibrium in steel production was published last year by Sauerwald and Hummitzsch(5).

In a process so complex as the manufacture of steel, the experimental study of every possible reaction which might occur among the

*The figures appearing in parentheses pertain to the references appended to the paper.

many individual components of metal, slag, refractories, and furnace gases would be a task of very great magnitude. If we add to this the necessity of determining the effects of such variables as temperature and composition upon each of the possible reactions, the problem becomes so large and complex that one might never expect to come to the end of it. At this point, however, the laws and methods of thermodynamics come to our rescue, assuring us that it is quite unnecessary to study every possible reaction, but rather every substance which is present. For, if the properties of every substance are accurately known, then the equilibrium conditions in every possible reaction may be calculated with precision. Thus, by the aid of thermodynamics we are able to simplify the problem to the study of a definite, limited number of substances instead of an almost unlimited number of reactions. The idea of simplifying anything by means of thermodynamics may seem a bit facetious to anyone who has thumbed the pages of textbooks on this subject. Nevertheless, the fundamental ideas of this science are simple, and that part of it which is essential to an understanding of its applications to steel making can be expressed without the use of complicated mathematical formulae.

A number of fundamental thermodynamic relationships will be employed in this paper and it will be well at the outset to review these briefly. For complete details of the thermodynamic methods the reader is referred to the text by Lewis and Randall(6). Let us write a general chemical reaction in which one molecule of A reacts with three of B to form two molecules of C.

$$A + 3\,B = 2\,C \qquad I$$

The "mass law" states that when equilibrium is attained there is a definite relationship among the three substances which is given by the expression:

$$K = \frac{(C)^2}{(A) \times (B)^3} \qquad II$$

in which K has a definite numerical value for any particular temperature and the terms (A), (B), (C) represent the chemical activities of the three substances.

This law, when stated as above in terms of the *activities* of the reacting substances, is perfectly general and there can be no question as to its validity(7). However, it is not always possible to

find the exact numerical value of the activity of each substance and for practical purposes it is necessary to introduce some approximations. Thus, for gases the activity is equal to the pressure; for pure solids and liquids the activity is equal to unity; in solutions the activity is approximately equal to the mol fraction. The first two of these approximations are quite accurate; the third, however, is only valid where the components of the solution are all very similar, as in a liquid mixture of similar metals or in basic slags containing similar oxides. In other cases, for example, in acid slags, the activity of a given component may differ greatly from its mol fraction, and in such cases the determination of the activity may become a problem of some difficulty.

In cases when full information on activity is lacking we must proceed on the assumption that it is proportional to mol fraction. In considering small percentages of dissolved substances in liquid steel, mol fraction and weight per cent are proportional, and activity is therefore proportional to percentage. In writing the mass law, therefore, we may let the parentheses of Equation II represent mol fraction or weight per cent. Then if we let (A) represent the percentage of substance A and (B) represent the mol fraction of substance B, we are merely assuming that the activities of these two substances are proportional to their weight percentage and mol fraction, respectively. In this form the "mass law" represents an extremely useful approximation.

The equilibrium constant of a reaction (K of Equation II) is directly related to the "standard change of free energy" for that reaction. The relationship is

$$\triangle F^\circ = -RT \ln K \qquad \text{III}$$

where $\triangle F^\circ$ is the change in free energy in the reaction when each substance is in a standard state (when its activity = 1), R is a constant, T the absolute temperature in degrees Kelvin, ($T^\circ K = t^\circ C + 273$) and ln K is the natural logarithm of the equilibrium constant. Using ordinary logarithms this becomes

$$\triangle F^\circ = -4.575\ T \log K \qquad \text{IV}$$

If we have the standard free energy of a number of substances we can easily calculate the equilibrium constant of any reaction occurring amongst them, as will be illustrated in later sections of this paper.

The free energy is related to the heat absorbed in the reaction, $\triangle H$, by the equation,

$$\triangle F^\circ = \triangle H - T\triangle S^\circ \qquad V$$

Where T is the absolute temperature and $\triangle S^\circ$ is the change in entropy. Concerning this last term it may be remarked that a great deal of progress has been made in recent years in determining the entropies of substances. A valuable summary of the data is contained in a recent bulletin of the Bureau of Mines by K. K. Kelley (8), to which we shall have frequent occasion to refer.

The effect of temperature upon the free energy is most simply expressed by substituting the numerical values of $\triangle H$ and $\triangle S$ in Equation V. A simple equation of this type can be used over a narrow range of temperature, say, from 1400 to 1800 degrees Cent., but is not accurate for extrapolating over wide ranges. This arises from the fact that both $\triangle H$ and $\triangle S$ are themselves functions of temperature and any accurate equation to cover a wide range must include additional numerical terms to take account of the heat capacities of the substances involved. A review of the data on heat capacities of substances which are of metallurgical importance will soon be available in a forthcoming bulletin by Kelley (9). The writer desires to thank Dr. Kelley for a copy of his manuscript in advance of publication.

The effect of temperature upon the equilibrium constant of a reaction is, of course, very closely related to its effect on free energy. Equation IV may be written

$$\log K = -\triangle F^\circ/4.575\ T \qquad VI$$

and substituting the value of $\triangle F^\circ$ from V we get

$$\log K = -\triangle H/4.575\ T + \triangle S/4.575 \qquad VII$$

so that within a limited temperature range where $\triangle H$ and $\triangle S$ remain nearly constant the logarithm of K is a linear function of the reciprocal of absolute temperature, and if we plot log K against 1/T we obtain a straight line. Plots of this sort are very useful and the method of plotting will be illustrated in a number of the graphs used in later parts of this paper.

The Free Energy of Gases

Before we can determine the free energy of most of the com-

pounds present in liquid steel and slag it is necessary to know the free energy, at steel making temperatures, of certain gaseous compounds. This necessity arises from the fact that much of our most reliable thermodynamic data on substances of metallurgical importance is based upon determinations of equilibrium in reactions of metals and their oxide with gases. Thus it was shown by the writer (10) in collaboration with D. W. Murphy that the free energy of ferrous oxide can be determined with accuracy from either of the following equilibria:

$$FeO + H_2 = Fe + H_2O;\ K = (H_2O)/(H_2)$$
$$FeO + CO = Fe + CO_2;\ K = (CO_2)/(CO)$$

The very satisfactory agreement between the two calculations would be impossible without dependable data on the free energies of steam, carbon monoxide and carbon dioxide. It was for this reason that the writer (11) felt compelled to review the data on these gases so as to obtain a more reliable set of free energy equations than had previously been published. Certain data of recent origin computed from spectroscopic observations may now be used, in connection with the precise calorimetric work of Rossini (12) at the Bureau of Standards, to improve still further the accuracy and reliability of these equations. The expressions used in the following work are based upon the spectroscopically determined entropies and heat capacities of Giauque and his associates (13), of Gordon and Barnes (14), and of Badger and Woo (15). The data are in substantial agreement with the results of equilibrium measurements, and the equations which follow are believed to be reliable within the temperature range stated.

It is a characteristic of mathematical formulae that if they are to be valid over a wide range of conditions they must be complicated. Thus the free energy of steam in the range 800 to 3000°K. is given by the equation.

$$H_2 + 1/2\ O_2 = H_2O;\ \triangle F.^\circ = -59251 + 0.87T\ \ln T - 0.000075T^2 + 408{,}000T^{-1} + 6.808T \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Such expressions may be simplified if we are content with having an expression which is applicable over a somewhat narrower temperature range. The following are derived from more complex equations of the type of (1). They are intended to be highly accurate at 1600 degrees Cent. and sufficiently precise for all practical purposes over the range 1200 to 2000 degrees Cent.

$$H_2 + 1/2\ O_2 = H_2O(g);\ \Delta F.^\circ = -60180 + 13.84T \quad (2)$$
$$CO + 1/2\ O_2 = CO_2;\ \Delta F.^\circ = -66430 + 19.94T \quad (3)$$
$$C(\text{graphite}) + CO_2 = 2\ CO;\ \Delta F.^\circ = +38300 - 40.09T \quad (4)$$
$$C(\text{graphite}) + 1/2\ O_2 = CO;\ \Delta F.^\circ = -28130 - 20.15T \quad (5)$$
$$C(\text{graphite}) + O_2 = CO_2;\ \Delta F.^\circ = -94560 - 0.21T \quad (6)$$

It is of interest to note that these equations which are applicable at the temperature of the open-hearth, are obtained from experimental observations at room temperature. Their reliability at high temperatures may be illustrated by comparing the dissociation of water vapor obtained from Equation (2) with that observed by Langmuir (16) and by von Wartenberg(17) at temperatures ranging from 1100 to 1984 degrees Cent. The dissociation constant is $K = (H_2)\ (O_2)^{1/2}/(H_2O)$, and its logarithm is found by dividing Equation (2) by 4.575T, which gives

$$\log K = -13154/T + 3.025$$

The comparison is shown in Fig. 1, from which it is evident that in this case the agreement between the theoretical line and the experimental data is practically perfect.

Oxygen in Liquid Iron

Oxygen is always present to some extent in steels—even in the deadest of the dead-killed variety. Its partial removal from the steel bath has formed the subject of many careful investigations. The deoxidation of steel, from the viewpoint of the completeness of the reactions and of the nature and effects of the nonmetallic products of these reactions, constitutes one of the most interesting problems in ferrous metallurgy. In establishing the limits attainable in the deoxidation of liquid steel the thermodynamic method finds one of its most useful metallurgical applications.

First, it is necessary to know something about the behavior and properties of oxygen itself in liquid iron. Le Chatelier(1) assumed that oxygen in liquid steel exists as molecules of FeO and that the solution of FeO in the liquid metal conforms to the law of mass action. He showed that this concept is in agreement with the known behavior of the gas-metal systems investigated by Sieverts(18) and that the solubility of uncombined oxygen as such in the liquid iron is negligibly small. This same assumption has been made by nearly all students of the open-hearth process and it is interesting to note that Le Chatelier's datum on the solubility of FeO in liquid iron of 1.1 per cent has not been materially altered by modern research.

In spite of the very general acceptance of the hypothesis that oxygen in liquid iron exists as dissolved FeO, no rigorous proof has yet been obtained and occasional doubts have been expressed. The constancy of the distribution ratio of oxygen between liquid iron and basic slags found by Herty and Gaines(19) and of the "manganese

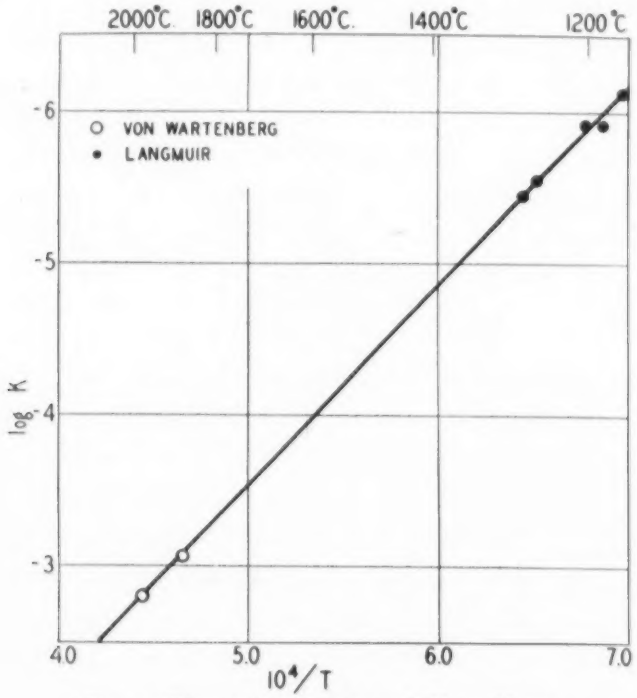

Fig. 1—Dissociation Constant of Water Vapor.

constant" which will be discussed later, certainly indicates the probable correctness of the assumption and the approximate applicability of the mass law. Recently the writer(20) has succeeded in obtaining experimental proof of the validity of the mass law as applied to oxygen in liquid iron. While it was not possible in these experiments to distinguish between FeO and a possible sub-oxide such as Fe_2O or Fe_3O, it was shown conclusively that the solute is an oxide containing one atom of oxygen per molecule.

This evidence was obtained from studies of the equilibrium in the reaction between liquid iron and steam, forming hydrogen and iron oxide which dissolves in the liquid iron. The experimental details have been described in the Journal of the American Chemical Society and it will be sufficient here to give a general outline of the method used and of the results obtained.

A charge of about 60 grams of electrolytic iron, previously

vacuum-melted, was held in a molten condition in a small induction furnace in a controlled gas stream for a length of time sufficient to insure the attainment of equilibrium. The melt was then solidified and its oxygen content determined by the vacuum fusion method. The composition of the gas in contact with the liquid iron was regulated by passing purified hydrogen through a saturator filled with

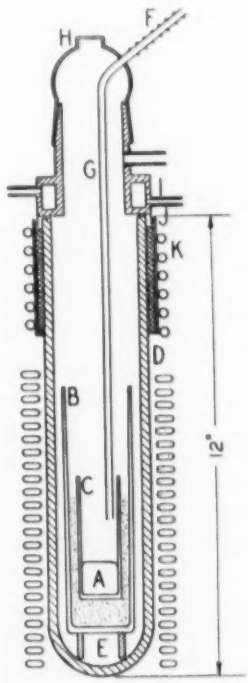

Fig. 2—Induction Furnace Used in Studying Equilibrium of Liquid Iron with Steam.

distilled water and maintained at constant temperature in a thermostat. The ratio of steam to hydrogen in the mixture was determined from the barometric pressure and the known vapor pressure of water. It was found that equilibrium between gas and metal was attained in 15 minutes but to avoid any uncertainties the majority of the heats were continued for one hour. The apparatus used in these experiments is shown in Fig. 2. A stream of hydrogen and water vapor of known composition entered through the tube FG and passed over the surface of the liquid iron A contained in the alumina or magnesia crucible C. Temperature measurements were made by sighting the optical pyrometer, which was calibrated at the melting point of pure iron, downward through the flat portion of the glass cap H.

The vacuum fusion equipment used in analyzing the specimens is shown in Fig. 3. This apparatus was originally patterned after that of Vacher and Jordan (21), though subsequent minor modifications have given it a somewhat changed appearance. We have found the volumetric method more reliable than the gravimetric and have used it exclusively. The analyses reported in Table I are in all

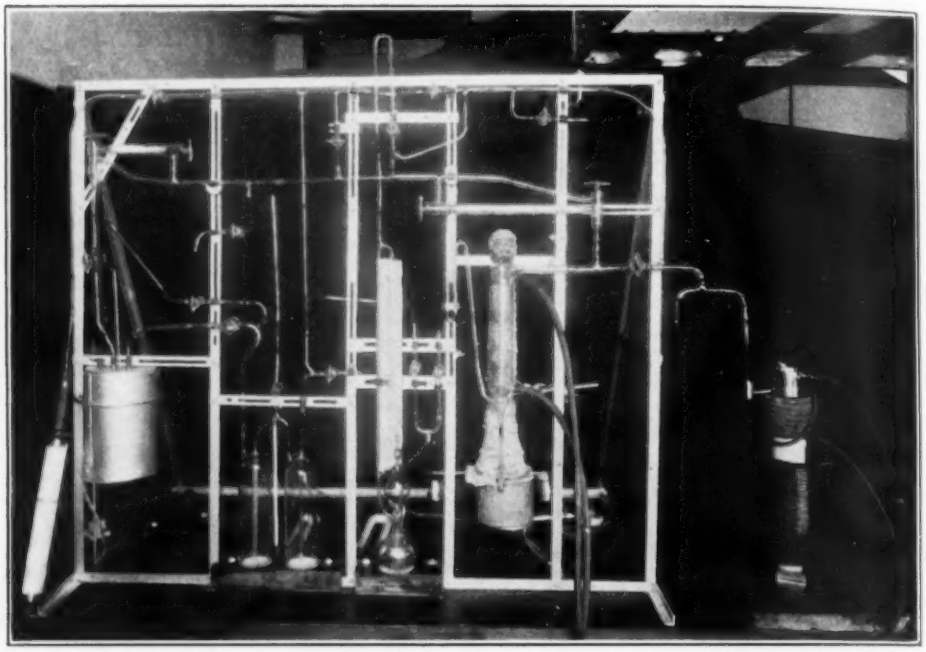

Fig. 3—Vacuum Fusion Apparatus Used in Determining the Percentage of Oxygen in the Specimens.

cases the results of two or more check determinations. At low percentages they are believed to be reliable within 0.001 per cent. At the highest concentrations (0.24 per cent) the analyses are good to ±0.004 per cent. The author wishes to express his thanks to M. G. Fontana for carrying out about twenty of the sixty-three analyses made during this investigation.

The results of the runs which were conducted at temperatures between 1600 and 1640 degrees Cent. are given in Table I, and are shown graphically in Fig. 4. In order to use these data to determine the constitution of the solution let us formulate the reaction in as general a manner as possible:

$$Fe_xO_y + yH_2 = xFe + yH_2O;\ K = \frac{(H_2O)^y.(Fe)^x}{(H_2)^y.(Fe_xO_y)}$$

Table I
Equilibrium in the Reaction of Liquid Iron with Steam

Run	Crucible	Time Minutes	Temperature Degrees Cent.	H_2O/H_2	Oxygen Per Cent
1	Al_2O_3	60	1600	0.0603	0.012
2	Al_2O_3	52	1605	0.0604	0.013
3	Al_2O_3	30	1610	0.0603	0.013
4	Al_2O_3	120	1600	0.0605	0.0115
5	Al_2O_3	60	1605	0.1216	0.027
6	Al_2O_3	120	1615	0.1215	0.025
7	Al_2O_3	30	1610	0.1222	0.027
9	Al_2O_3	60	1610	0.262	0.057
11	Al_2O_3	60	1620	0.263	0.056
12	MgO	60	1620	0.262	0.058
13	MgO	60	1620	0.477	0.116
15	MgO	90	1625	0.473	0.113
16	MgO	40	1635	0.473	0.113
17	MgO	15	1625	0.474	0.117
18	MgO	60	1620	0.261	0.059
21	MgO	60	1620	0.964	0.242
23	BeO	60	1610	0.979	0.212
26	MgO	60	1600	0.691	0.155

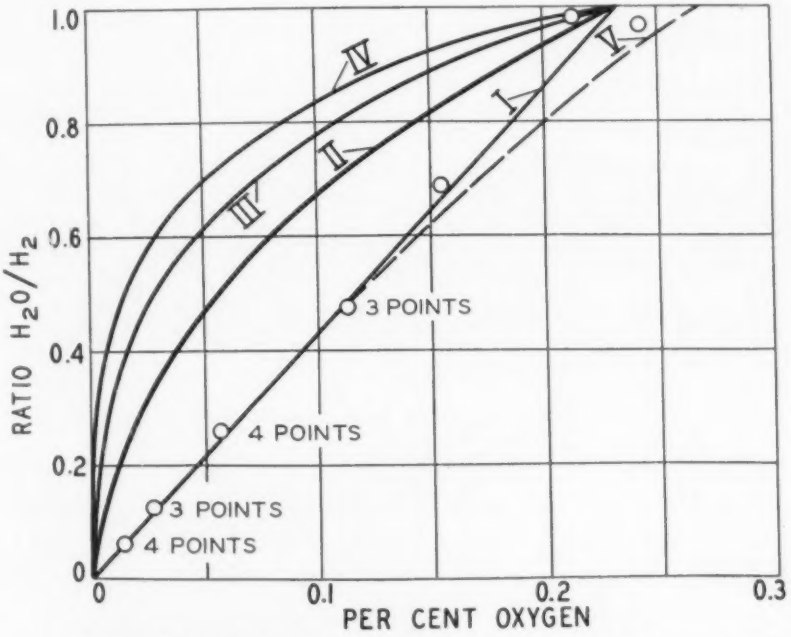

Fig. 4—Equilibrium Ratio H_2O/H_2 as a Function of Oxygen in the Melt. (1620 Degrees Cent.)

In these dilute solutions the concentration of iron is practically unity; hence $(Fe)^x = 1$. Further, the concentration of Fe_xO_y is proportional to the percentage of oxygen and therefore,

$$[(H_2O)/(H_2)]^y = K' \times \text{per cent oxygen}$$

This equation states that if $y = 1$, the percentage of oxygen in the melt will be proportional to the ratio $(H_2O/(H_2)$ and experimental

points should fit a straight line (Curve I). If the solute has a more complex formula so that y = 2, 3, or 4, then the percentage of oxygen should be proportional to the square, cube or fourth power of the steam-hydrogen ratio and the data should fit a curve of the type II, III or IV. The fact that they fit a straight line is to be regarded as

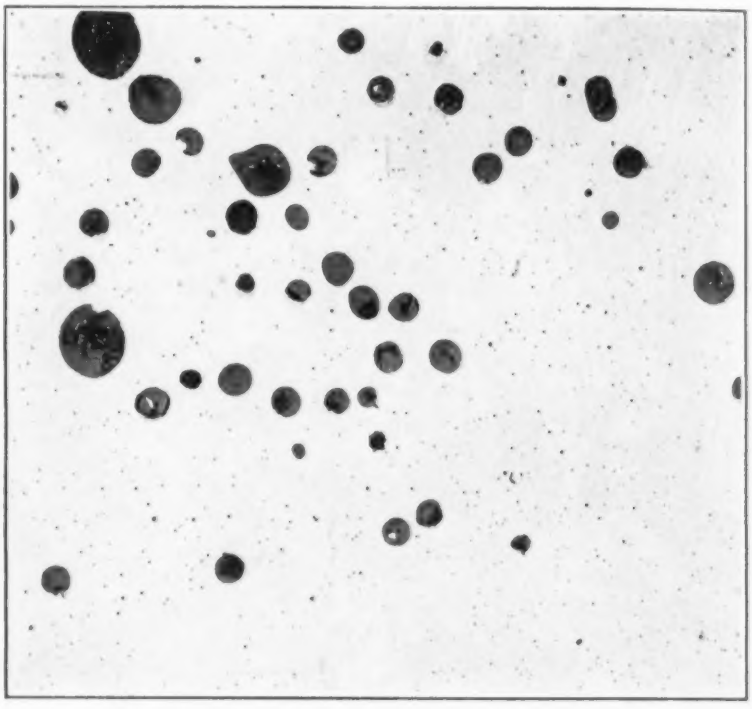

Fig. 5—Large FeO Inclusions Near Top of Heat 21 and Very Small Inclusions Typical of the Series. Unetched × 100.

definite proof that y = 1, although obviously it tells us nothing regarding x. The solute may, therefore, be FeO, Fe_2O, Fe_3O, or Fe_xO, but since these are virtually indistinguishable thermodynamically it is quite unnecessary to settle this point. We may, therefore, write its formula FeO with the fullest assurance that any calculations based upon this formula will not be appreciably in error, even if future investigation should show that the true formula is Fe_2O or Fe_3O.

Now, although the data as plotted are adequately represented by the straight line of Curve I, it is found that when corrections are applied (by a method described elsewhere) to bring each point to 1620 degrees Cent., the resultant data are better represented by a line of slight curvature (Curve V). This curvature is necessitated also

by the fact that the line must pass to the right of the two points above 0.2 per cent oxygen. These two heats (21 and 23) ejected ferrous oxide on cooling and the analytical result is therefore known to be low. The excess of ferrous oxide above that corresponding to the solubility at the melting point is thrown out of solution as the melt cools. This is shown in process of occurring in Fig. 5 showing large

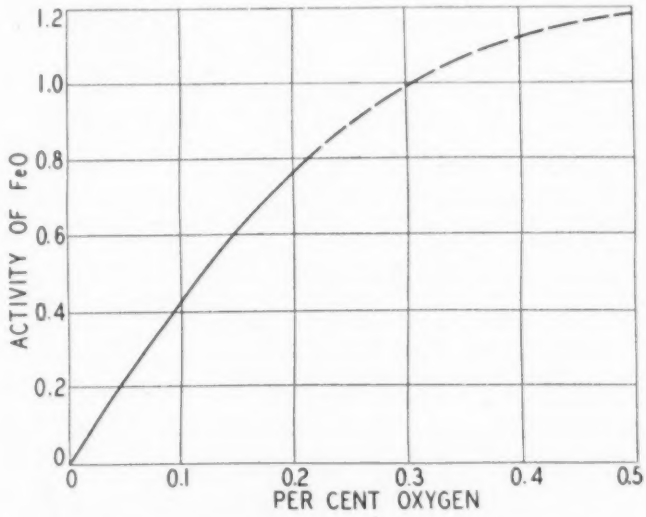

Fig. 6—Relation Between Activity of Ferrous Oxide and Per Cent Dissolved Oxygen.

oxide inclusions at the extreme top of Ingot 21 and the smaller distribution throughout the rest of the ingot. In Ingot 23, all of the excess FeO above 0.21 per cent oxygen was liberated before solidification was complete, and the distribution was uniform throughout the ingot. Similarly in all the other ingots examined the distribution was uniform. It is necessary, therefore, in any experiments involving the determination of oxygen above 0.20 per cent to provide a faster rate of cooling than was used in these experiments (about 175 degrees Cent. per minute).

To return to Curve V of Fig. 4, the slight departure from the straight line indicates that the solution does not precisely conform to the laws of the ideal solution. This is not at all surprising and the amount of deviation from the ideal solution law is not great. It means, however, that in applying the mass law to reactions involving dissolved ferrous oxide, we must use the activity function rather than the concentration. It will be convenient to define the activity of ferrous oxide in liquid iron by specifying that at low concentrations

Table II
Activity of Ferrous Oxide in Liquid Iron

Oxygen Per Cent	FeO Per Cent	Activity Coefficient	Activity *a*FeO
0.01	0.045	1.00	0.045
0.02	0.090	1.00	0.090
0.05	0.224	0.98	0.220
0.10	0.449	0.96	0.429
0.15	0.674	0.91	0.613
0.20	0.898	0.86	0.770

its activity is equal to its per cent by weight. That is, if the melt contains 0.01 per cent FeO, then its activity is 0.01. At higher concentrations the activity will be somewhat less than the percentage (on account of the curvature of Curve V), and a table of activities can be deduced from the equilibrium measurements. This was done in the previous publication, from which Table II is quoted. Here the activity coefficient is the ratio of activity to percentage, and its departure from unity represents the deviation of the solution from the ideal. The activity of FeO is plotted against the per cent oxygen in Fig. 6. Above 0.2 per cent oxygen the line is an extrapolation. The true equilibrium constant of the reaction which by the mass law must remain constant at constant temperature is,

$$K = \frac{(H_2O)\ (Fe)}{(H_2) \times (a\text{FeO})}$$

The variation of this constant with temperature was determined over the range 1550 to 1770 degrees Cent. The experimental data are shown in Fig. 7 in which the logarithm of the equilibrium constant is plotted against the reciprocal of the absolute temperature. The line is drawn straight for theoretical reasons and because the temperatures of the three points at the extreme right are probably too low. The equation of this line is,

$$\log K = 6200/T - 3.28$$

The slope of the curve corresponds to a heat evolution of 28,400 calories per mol. The free energy change in the reaction is obtained by multiplying the above expression for log K by —4.575T. This gives,

$$\text{FeO (\% in Fe)} + H_2 = \text{Fe}(l) + H_2O;\ \Delta F^\circ = -28400 + 15.0T \quad (7)$$

The symbol (% in Fe) after FeO will be interpreted to mean that

this substance is dissolved in the bath and that its activity is defined in terms of its per cent by weight. By combining Equations (7) and (2) we obtain an expression for the change in free energy in the formation of dissolved ferrous oxide from its elements.

$$Fe(l) + 1/2\ O_2 = FeO\ (\%\ in\ Fe);\ \Delta F^\circ = -31780 - 1.16T \quad (8)$$

Some useful information is contained in the data represented by Table II and Equation 8. Let us use these data to calculate the

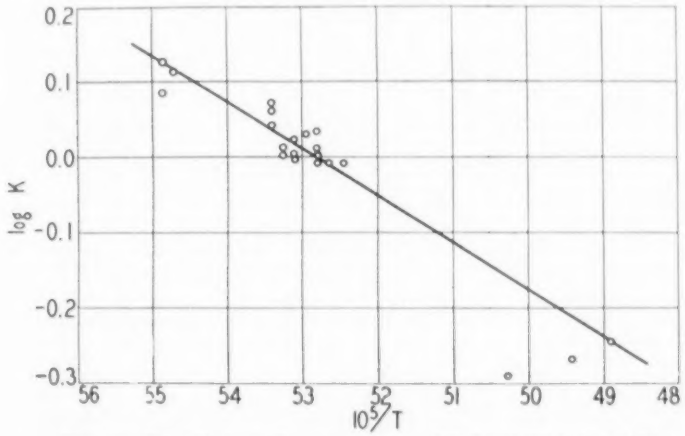

Fig. 7—Equilibrium Constant, $K = (H_2O)/[(H_2)\ (a\ Fe\ O)]$ as a Function of Temperature.

oxygen pressures of liquid iron at various temperatures and percentages of oxygen. Dividing Equation 8 by —4.575T, we find

$$K = (a\text{FeO})/(O_2)^{1/2};\ \log K = 6950/T + 0.254$$

In this equation (aFeO) is the activity of ferrous oxide as given in Table II and (O_2) is the oxygen pressure in atmospheres. The calculated values of the oxygen pressure are given in Table III. It is to be observed that the highest pressure in this table, 168×10^{-10} atmospheres is approximately 10^{-5} millimeters, which is about the limit of the best vacuum pump. This demonstrates the futility of attempting to remove oxygen from carbon-free iron by melting in vacuum.

Table III
Oxygen Pressures of Liquid Iron-Oxygen Solutions

Temperature Degrees Cent. =		1550	1600	1650	1700
Oxygen Per Cent	FeO Activity	Oxygen Pressure (atm. $\times 10^{-10}$)			
0.01	0.045	0.15	0.24	0.37	0.57
0.02	0.090	0.60	0.96	1.48	2.29
0.05	0.220	3.6	5.7	8.9	13.6
0.10	0.429	13.7	21.7	33.8	52.0
0.20	0.770	44.0	70.0	109.0	168.0

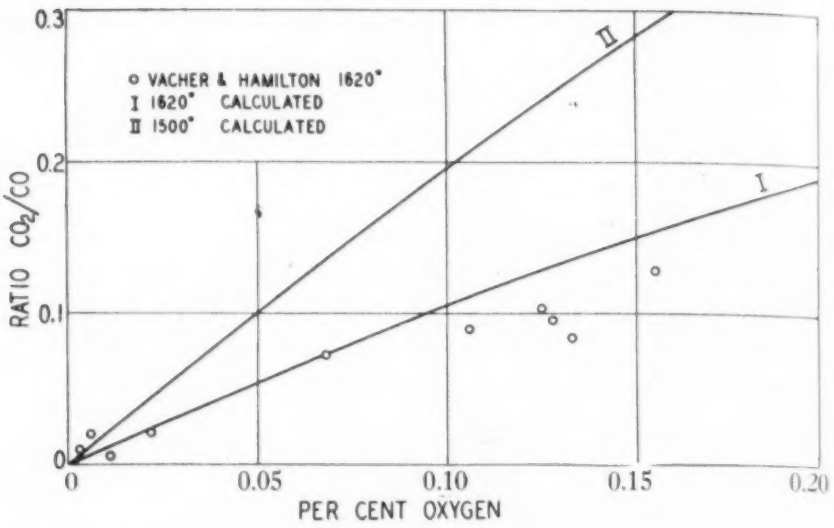

Fig. 8—Composition of Equilibrium Gas as Related to Oxygen Content.

By combining Equations 3 and 8 we obtain a very useful expression:

$$FeO\ (\%\ in\ Fe) + CO = Fe(l) + CO_2;\ \Delta F^\circ = -34650 + 21.10T \quad (9)$$

This equation will be used to calculate the ratio of CO_2/CO in equilibrium with liquid iron of varying oxygen content. Dividing Equation 9 by $-4.575T$ we find,

$$K = (CO_2)/[(CO)\ (a FeO)];\ \log K = +7573/T - 4.61$$

The ratio $(CO_2)/(CO)$ is given in Table IV for two temperatures, 1500 and 1620 degrees Cent. The first is approximately the temperature of solidification of rimming steel and the ratios in this column should correspond to the ratios of the two gases in the gases evolved from a solidifying open ingot. The ratios at 1620 degrees Cent. may be compared directly with the ratios observed by Vacher and Hamilton (22). Although these investigators state specifically that their gas analyses were only approximate, it is evident from Fig. 8 that their ratios agree fairly well with those calculated from Equation 9.

In applying our thermodynamic calculations to reactions involving slag we require the free energy of pure liquid ferrous oxide. The determination of this quantity is the object of further experimental work which is now in progress. Pending the completion of these experiments, we will employ an approximate equation found in

Table IV
Ratio CO_2/CO in Equilibrium with Liquid Iron-Oxygen Solutions

Oxygen Per Cent	FeO Activity	Temperature Degrees Cent. = 1500 CO_2/CO	1620 CO_2/CO
0.005	0.022	0.010	0.0055
0.01	0.045	0.020	0.011
0.02	0.090	0.041	0.022
0.05	0.220	0.100	0.054
0.10	0.429	0.196	0.105
0.20	0.770	0.352	0.189

the following manner from an extrapolation of the data discussed above.

Since the solubility of FeO in liquid iron is known with a fair degree of accuracy from the work of Herty(19) and of Körber,(23) the extrapolated data of Table II, shown in Fig. 6, may be used to find the activity of FeO in the saturated solution. The result is

$$\log (a\text{FeO}) \text{ (saturated)} = -3200/T + 1.70$$

Since the free energy of liquid FeO is approximately equal to its free energy in the saturated solution, the above is equivalent to the free energy equation:

$$\text{FeO}(l) = \text{FeO (\% in Fe)}; \Delta F^\circ = 14600 - 7.76T \qquad (10)$$

When this is combined with Equation 8 we find

$$\text{Fe}(l) + \tfrac{1}{2}\,O_2 = \text{FeO}(l)\ \Delta F^\circ = -46380 + 6.60T \qquad (11)$$

Carbon in Liquid Iron

The nature of the solution of carbon in liquid iron has long been of interest to metallurgists and numerous attempts have been made to throw light upon this problem by the application of thermodynamic methods. The constitution of a solid or liquid solution can be determined with the aid of certain formulae and assumptions, provided data of sufficient quantity and accuracy are available. Now, in the case of the iron-carbon system there is no dearth of data—so far as quantity is concerned. However, the degree of concordance among various sets of data leaves much to be desired, and the thermodynamic deductions which have been made from these data cannot be accepted with finality until the data themselves are more thoroughly substantiated. Indeed, there is such a variety of data available on

this system that one might prove almost any hypothesis regarding the constitution of solutions of carbon in iron by exercising a judicious selection of data.

The situation may be illustrated by a comparison of the conclusions recently reached by several metallurgists who have applied thermodynamic methods to the study of the constitution of the solid and liquid solutions. Jeffery(24) finds that "all parts of the diagram which contain austenite lead to the conclusion that it consists of monatomic molecules of carbon dissolved in monatomic molecules of gamma iron." On the other hand, Yap, Chu-Phay,(25) whose first conclusion agreed with that of Jeffery, subsequently decided that the solute in austenite is a carbide. Körber and Oelsen,(27) using the thermal data of Oberhoffer and Grosse,(28) showed that the A_3 line could be calculated on the assumption that the solute in austenite is Fe_3C. Had they employed Klinkhardt's(29) thermal data their results would have been altogether different, and they would doubtless have discovered that the solute in austenite is atomic carbon. It is worthy of note that all of the data lead to the conclusion that the solute in austenite contains only one atom of carbon per molecule. That is, its formula is Fe_xC and not Fe_xC_2 or Fe_xC_3. Various sets of data are satisfied by values of x ranging from zero to three, and we must conclude with Austin(30) that the uncertainties in the data are so great that no further conclusions can be drawn.

Precisely the same uncertainties are found in data pertaining to the liquid solution. Again Jeffery finds that "the liquid solution in equilibrium with the solid solution . . . . appears to consist of monatomic carbon molecules dissolved in monatomic iron molecules." Yap, Chu-Phay(26) in discussing the composition of the liquid solution at 1600-1700 degrees Cent. states that "the Fe_3C is practically undissociated, a conclusion which we would have arrived at long ago from free energy considerations." Körber and Oelsen have shown how the several sets of data on the solidus and liquidus curves may be compared with the theoretical relationships calculated from the heat of fusion of iron. Their Fig. 3 is reproduced in our Fig. 9. Curve I is calculated from thermal data, Curves II and IV indicate the results of two series of experimental data combined with the assumption that the solute in both austenite and liquid is Fe_3C. Curves III and V show the same data in terms of atomic carbon as the solute. These calculations do not permit us to state with certainty whether the solute is C or Fe_3C. They do show that the solute molecules

contain only one atom of carbon and from zero to three atoms of iron. Körber and Oelsen consider Curve 4 the best representation of the experimental data, and interpret this as indicating that the solute is Fe_3C, which at the higher carbon concentrations is partially dissociated into Fe and C.

The data of Ruff and Borman(31) on the boiling points of iron and of iron-carbon alloys at low pressures may be used to calculate

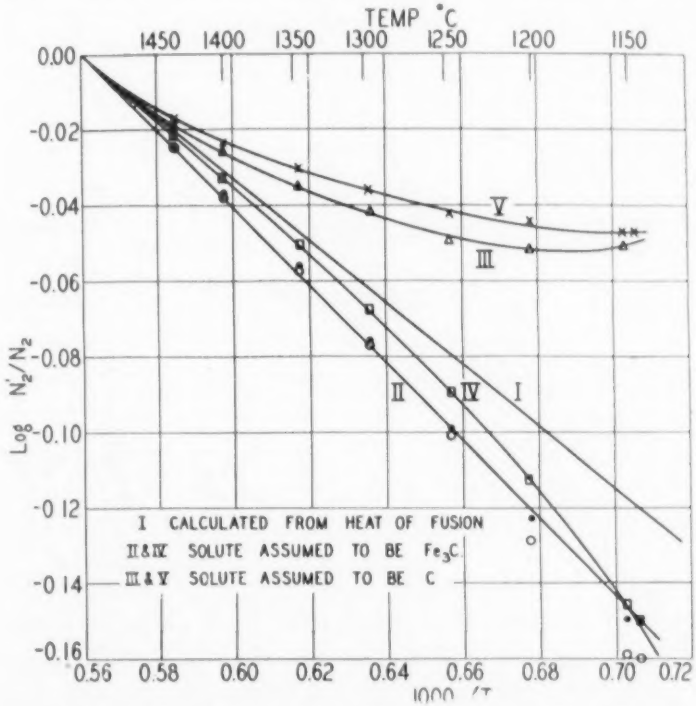

Fig. 9—Comparison of the Melting Points of Iron-Carbon Alloys with the Theoretical Line (Körber and Oelsen).

the molecular formula of the solute. They found that at 36 millimeters pressure the boiling point of an alloy containing 7.4 per cent carbon is 2650 degrees Cent. At the same pressure the boiling point of pure iron was 2450 degrees Cent. From the latter point, Millar (34) has deduced an equation for the vapor pressure of pure iron from which we find 92 millimeters at 2650 degrees Cent. The mol fraction of free iron in the alloy is, therefore, $36/92 = 0.39$. Now, the mol fraction of free iron in an alloy containing 7.4 per cent carbon depends upon the molecular formula of the carbide present, as shown in Table V. Of these possible carbides, the only one which permits a mol fraction of iron approximating that deduced from the vapor pressure measurements is Fe_2C. We therefore conclude that

on the basis of Ruff and Borman's data the average composition of the solute at 2650 degrees Cent. is Fe_2C. Of course, this tells us nothing as to the constitution of the solution at 1600 degrees Cent.

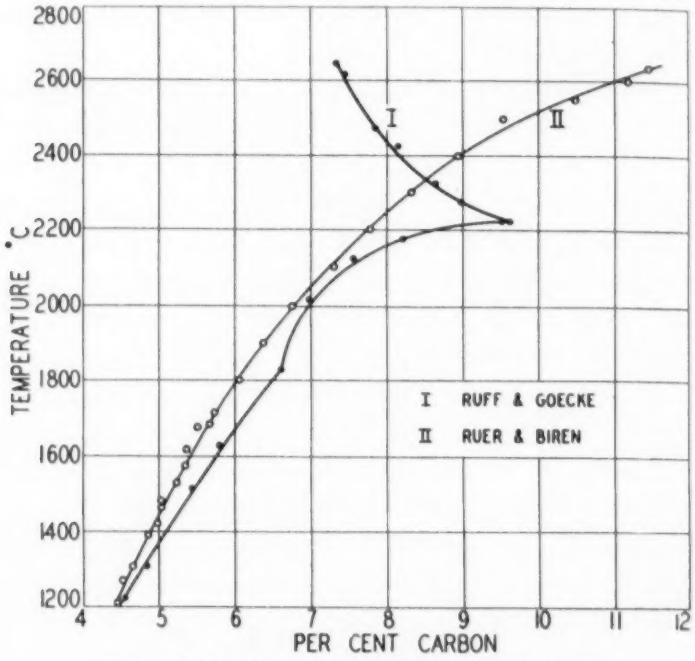

Fig. 10—Solubility of Graphite in Liquid Iron.

No one has yet attempted to determine the constitution of the liquid iron-carbon alloys from that part of the diagram which shows the solubility of carbon in liquid iron. The data of Ruff and Goecke (32) and of Ruer and Biren(33) are shown in Curves I and II, respectively, of Fig. 10. The disagreement between these results at the highest temperatures calls for further experimental studies. The fact that the solubility of graphite in iron exceeds its proportions in the compound Fe_3C is sufficient proof that the latter is not the only solute present.

In order to see whether the data are capable of deciding which of the possible carbides of iron is present, let us formulate the hypothetical reaction and its equilibrium constant.

$$C(\text{graphite}) + x\ Fe(l) = Fe_xC(\text{dissolved}); K = (Fe_xC)/(Fe)^x$$

Table V

Mol Fraction of Free Iron in 7.4 Per Cent Carbon Alloy

Assumed Solute	C	FeC	Fe_2C	Fe_3C	FeC_2	Fe_4C_2	Fe_5C_2
Mol fr. Fe	0.73	0.63	0.41	0	0.81	0.58	0.28

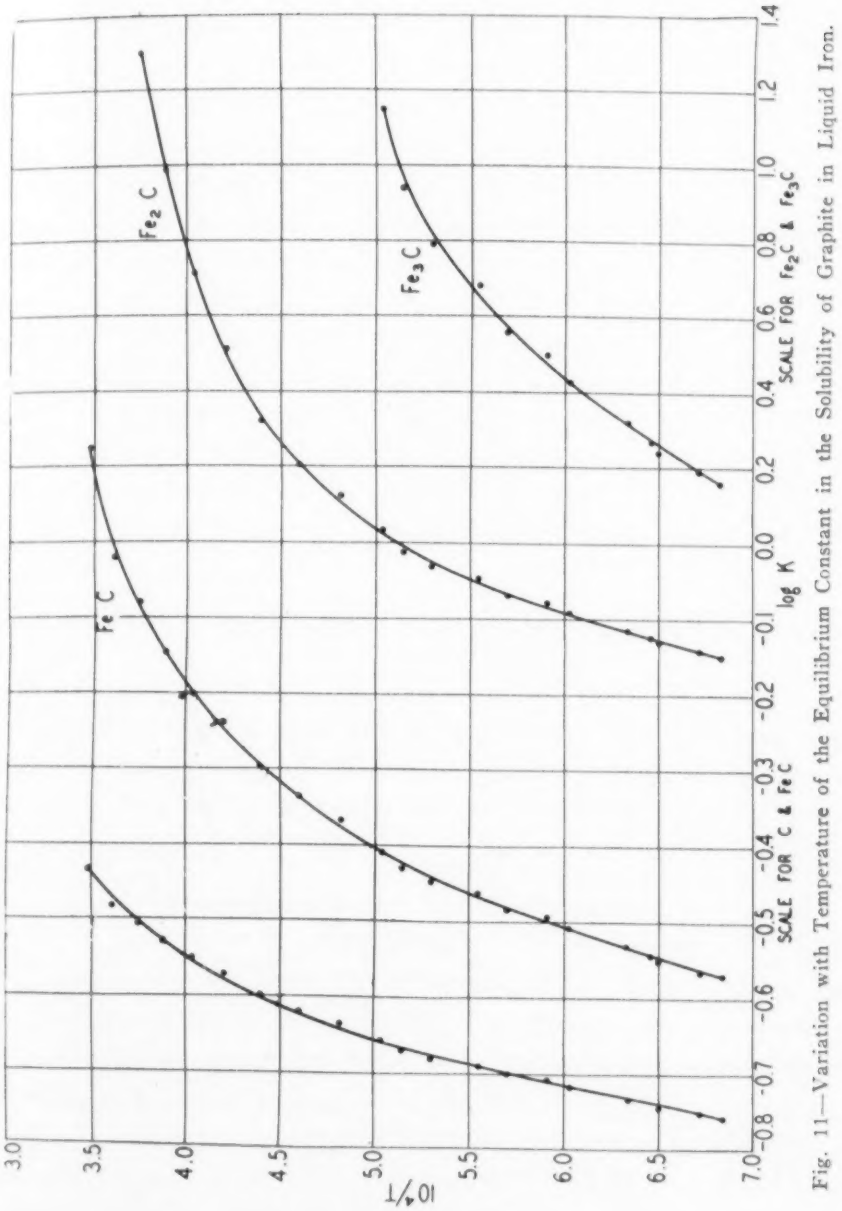

Fig. 11—Variation with Temperature of the Equilibrium Constant in the Solubility of Graphite in Liquid Iron.

where (Fe_xC) and (Fe) are the mol fractions, respectively, of carbide and of free iron. Now, if we plot the logarithm of K against the reciprocal of the absolute temperature for each value of x, we obtain a series of curves shown in Fig. 11. If any one of these curves had been a straight line, the conclusion would have been justified that this represented the true composition of the solute. Since all the lines are strongly curved, the more reasonable conclusion is that the

solute cannot be represented by a constant formula and that its average composition varies both with temperature and with the composition of the melt.

This conclusion is not at all out of line with our present knowledge regarding the behavior of "solvated" solutes—substances which form compounds with the solvent material. Qualitatively, the effect of a decrease in the carbon content of the solution must be an increase in iron content of the solute. Probably a decrease in temperature would have the same effect. Therefore, if the solute has an average composition at 2650 degrees Cent. corresponding to Fe_2C when the carbon content of the solution is 7.4 per cent, then at 1600 degrees Cent. and low carbon percentages it is very probable that its average composition is more nearly Fe_3C. In the calculations of the following section it will be assumed that the principal form of carbon in liquid steel and in austenite is Fe_3C.

Reactions of Dissolved Iron Carbide with the Oxides of Iron and of Carbon

Several chemical reactions involving dissolved iron carbide have been studied, both in austenite and in liquid iron. The best known of these is the carburizing reaction whose equation and equilibrium constant are written as follows:

$$Fe_3C \text{ (in austenite)} + CO_2 = 3\ Fe \text{ (in austenite)} + 2\ CO$$

$$K = \frac{(Fe)^3\,(CO)^2}{(Fe_3C)\,(CO_2)}$$

The equilibrium constant is obtained from data on the carbon content of steels in equilibrium with known atmospheres of CO and CO_2. This equilibrium was studied by Johansson and von Seth(35) and by Takahashi(36) in 1926. The results of the two investigations were in marked disagreement and it was impossible to draw from them any final conclusions as to the free energy of iron carbide. The recent investigation of Dünwald and Wagner,(37) using an entirely different method, yielded results which were in good agreement with those of Takahashi and apparently of even higher accuracy. Still another method was employed by Becker,(38) whose results, after certain minor corrections, are substantially in accord with both of the above.

The whole problem of the chemical reactions of cementite and its solid solution in austenite is being made the subject of an investigation in which the author is fortunate in having the collaboration of S. F. Urban. Since, at the present moment, we are primarily interested in the liquid solution, our remarks concerning the solid solution will be confined to presenting Fig. 12 which contains the results

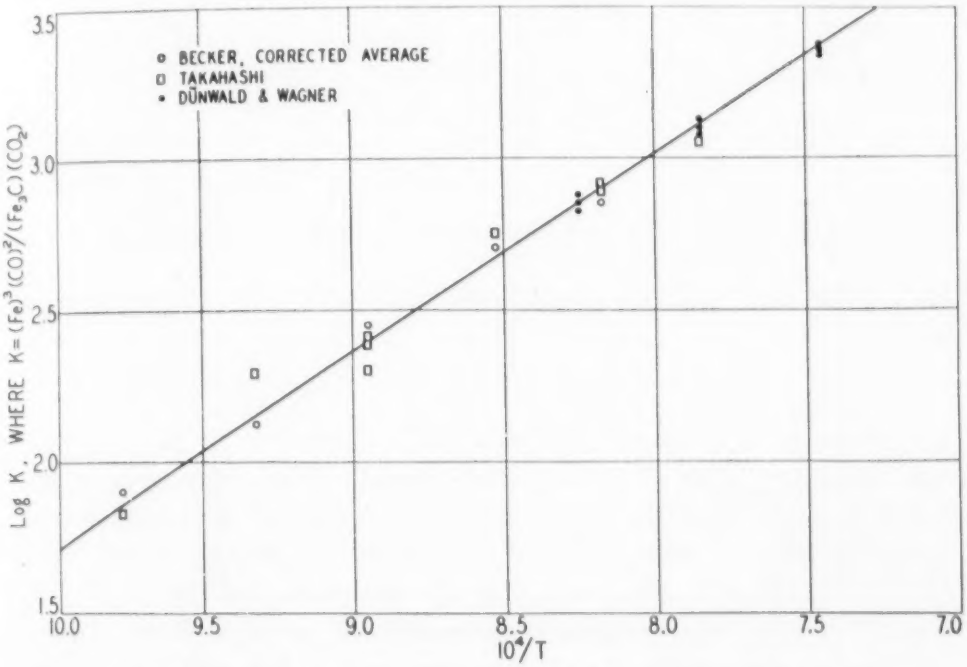

Fig. 12—Equilibrium Between Austenite and the Oxides of Carbon.

of the calculations on the above reaction. In this figure the logarithm of the equilibrium constant is plotted against the reciprocal of the absolute temperature and the straight line is represented by the expression:

$$\log K = 6300/T + 8.05$$

from which we may write the free-energy equation:

$$Fe_3C(\text{in austenite}) + CO_2 = 3\ Fe(\text{in austenite}) + 2\ CO;$$
$$\Delta F^\circ = 28800 - 36.80\ T \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Now, before Equation 12 can be applied to the liquid solution, we must have two additional equations showing the free energy change in the transfer of carbide and of gamma iron from austenite to liquid. Selecting from the many data of the iron-carbon diagram

the liquidus of Ruer and Goerens(39) and the straight line solidus, it is found that the equilibrium ratio of the mol fraction of Fe_3C in liquid iron to that in austenite at the same temperature is practically constant and equal to 3.6. Then the free energy change is simply —4.575 T log 3.6, and we have,

$$Fe_3C(\text{in austenite}) = Fe_3C(\text{in liq.Fe}); \Delta F^\circ = -2.55\ T \quad \ldots\ldots (13)$$

The ratio of the mol fraction of iron in the liquid to its mol fraction in austenite is given by Körber and Oelsen(27) as:

$$\log X'/X = -822.6\sqrt{T} + 0.4593$$

which we multiply by —4.575 T to obtain the free energy equation,

$$Fe(\gamma) = Fe(l); \Delta F^\circ = +3760 - 2.10\ T \quad \ldots\ldots (14)$$

By combining Equations 12, 13 and 14, we find for the reaction in liquid iron:

$$Fe_3C(\text{in 1 Fe}) + CO_2 = 3\ Fe(l) + 2\ CO; \Delta F^\circ = 40080 - 40.55\ T \quad \ldots (15)$$

Now, it happens that the equilibrium constant of this reaction was measured by Vacher and Hamilton(22) although this was not the main purpose of their investigation. From their data the author (40) was able to show that at 1620 degrees Cent. the equilibrium constant of the reaction is in the neighborhood of 12,000. For comparison the free energy equation is solved for a temperature of 1893 degrees K. and we find,

$$K = \frac{(CO)^2\,(Fe)^3}{(Fe_3C)\,(CO_2)}; \quad K_{1893} = 17{,}000.$$

The agreement is well within the limits of error of the several sets of data involved and serves to increase one's confidence in the validity of the thermodynamic methods employed.

It is customary to express carbon concentrations in per cent, rather than in the more complicated mol fractions. It is also permissible to write equilibrium constants in terms of percentages so long as this practice is confined to studies of low-carbon steels. For at low carbon contents the per cent carbon is equal to the mol fraction of carbide multiplied by a constant factor of 21.5, and the mol fraction of iron is practically unity. To convert the free energy equations from mol fraction of carbide to per cent carbon we add a purely formal transformation equation:

$$Fe_3C(\text{mol fr.}) = 3\ Fe(\text{mol fr.}) + C(\%);$$
$$\Delta F^\circ = -4.575\ T \log 21.5 = -6.10\ T \ldots\ldots (16)$$

Then equation 15 may be put into a more convenient form simply by subtracting Equation 16, which gives:

$$C(\%\text{ in l. Fe}) + CO_2 = 2\ CO;\ \Delta F^\circ = 40080 - 34.45\ T \ldots\ldots (17)$$

The similarity between this and Equation 4 is at once obvious. By combining the two, we obtain an expression for the free energy of carbon dissolved in liquid iron relative to graphite. It must be remembered that this equation applies to low carbon percentages only and should certainly not be employed above about 0.50 per cent carbon.

$$C(\text{graphite}) = C(\%\text{ in l. Fe})\ \Delta F^\circ = -1780 - 5.64\ T \ldots\ldots (18)$$

Among the many chemical reactions which occur during the making of a heat of steel, none has received more careful study than the carbon-oxygen reaction,

$$C(\text{in Fe}) + FeO(\text{in Fe}) = Fe(l) + CO\ (g)$$

This is the reaction by which carbon is eliminated from the bath and the evolution of carbon monoxide gas is the cause of the boil. In general, the evolution of carbon monoxide has been found to cease when the product of per cent carbon times per cent FeO falls to about 0.01 to 0.03. The question of whether or not this product represents a true equilibrium has received the attention of many investigators. According to Styri's(2), (41) calculations the equilibrium conditions would correspond to a product of carbon times FeO of about 0.0005. This is also approximately the value found experimentally by Kinzel and Egan.(41) More recently Vacher and Hamilton(22) found 0.011 at 1620 degrees Cent., which is approximately equal to the lower limit of the open-hearth results. To calculate the equilibrium constant from the free energy equations let us first combine Equations 5, 8, and 18 to obtain,

$$Fe(l) + CO = FeO(\%\text{ in Fe}) + C(\%\text{ in Fe});$$
$$\Delta F^\circ = -5430 + 13.35\ T \ldots\ldots\ldots\ldots\ldots\ldots (19)$$

According to this equation, the equilibrium constant at 1620 degrees Cent. (1893°K.) is,

$$\frac{(\%FeO)\ (\%C)}{(CO)} = 0.005$$

A summary of the various calculated and experimental values of this constant is given in Table VI. It is to be noted that the newly calculated value is ten times as large as Kinzel and Egan's experimental result and about one-half that of Vacher and Hamilton's. Considering the many sets of experimental data that are involved, the agreement with the results of Vacher and Hamilton is not exceptionally bad. It has been shown, moreover, that their data are quite consistent from the point of view of gas compositions and we may confidently anticipate that further research on the several reactions involved will bring the calculated and experimental values into even better agreement.

Table VI
Values of the Carbon FeO Product in Liquid Iron

Author	Method	Per Cent C × Per Cent FeO
Styri(41)	Calculated	0.0005
Kinzel and Egan(41)	Experimental	0.0005
Herty and Associates(19)	Open-Hearth	0.01 to 0.03
Feild(42)	Kinetics	0.006 to 0.014
Gaines(41)	Calculated	0.00098
Larsen(43)	Calculated	0.0016
Vacher and Hamilton(22)	Experimental	0.011
Chipman	Calculated	0.005

Alloy Elements

Many of the common alloy elements are entirely soluble in liquid iron and form no compounds with iron. In such cases the solution is probably very nearly "ideal," which means simply the activity of the dissolved metal is equal to its mol fraction. An expression for the free energy of such a metal at low concentrations is easily obtained.

Let M be any metal which forms an ideal solution in iron, and w its atomic weight. Then if c is some small percentage of the metal in iron and N its mol fraction,

$$N = \frac{c/w}{c/w + (100-c)/55.84}$$

At low percentages of M this simplifies to:

$$N = 0.5584\, c/w$$

Then, at unit concentration the mol fraction is 0.5584/w. The

change in free energy in diluting the pure liquid metal from a mol fraction of 1 to a mol fraction N is,

$$\Delta F^\circ = 4.575\ T \log N,$$

Therefore, in diluting to a mol fraction of 0.5584/w, it is:

$$M(1) = M(\%\text{ in Fe});\ \Delta F^\circ = 4.575\ T \log (0.5584/w) \quad \ldots\ldots (20)$$

This equation is applicable to vanadium, chromium, manganese, nickel, and cobalt and for these metals it is probably quite exact. With somewhat less certainty, it may also be used for tungsten and molybdenum and in general as a first approximation for metals which are soluble in all proportions in liquid iron. The following expressions, based upon Equation 20, will be used in later sections of this paper:

$$Mn(1) = Mn(\%\text{ in Fe});\ \Delta F^\circ = -9.11\ T \quad (21)$$
$$Ni(1) = Ni(\%\text{ in Fe});\ \Delta F^\circ = -9.21\ T \quad (22)$$
$$Cr(1) = Cr(\%\text{ in Fe});\ \Delta F^\circ = -9.01\ T \quad (23)$$

It should be noted that, while these equations are strictly valid only at low concentrations, the above elements have atomic weights not very different from iron, so that weight per cent and mol per cent are nearly equal and the equations can be used even in calculations relating to high alloy steel.

In cases when the alloy element in the pure state is a solid at steel-making temperatures, it is convenient to have an equation expressing the over-all change in free energy in going from the solid metal to the dilute solution in iron. As an example, pure chromium melts at 1800 degrees Cent. and therefore at this temperature, which is 2073°K., the free energies of solid and liquid are identical. The effect of temperature upon the free energy depends upon the heat of fusion, which in the case of chromium is not known with precision; but since the heat of fusion divided by the absolute melting temperature is about 2.1 for most metals we may estimate it as about 4350 calories per gram atom. Then the free energy change is,

$$Cr(s) = Cr(1);\ \Delta F^\circ = 4350 - 2.10\ T \quad \ldots\ldots (24)$$

Now, adding Equations 23 and 24 we find,

$$Cr(s) = Cr(\%\text{ in Fe});\ \Delta F^\circ = 4350 - 11.11\ T \quad \ldots\ldots (25)$$

In precisely the same way we find the following equation for vanadium:

$$V(s) = V(\%\text{ in Fe});\ \Delta F^\circ = 4200 - 11.07\ T \quad \ldots\ldots (26)$$

The change in free energy when silicon is dissolved in liquid iron is subject to some uncertainties on account of the formation of the compound FeSi, whose free energy is not known. If we had the heat of formation of this compound, this would serve as a reasonable approximation, but the only actual data on the compound appear in the work of Haughton and Becker(44) on the phase boundaries of the system iron-silicon. From the shape of their curve it is evident that the compound dissociates in the liquid phase and the following equation is based upon the reasonable guess that the dissociation amounts to about 50 per cent at the melting point (1410 degrees Cent.).

$$Si(1) = Si(\%\text{ in Fe});\ \Delta F^\circ = -7000 - 7.78\ T \quad \ldots\ldots\ldots\ldots\ldots\ldots (27)$$

It would be possible to write out the same sort of approximate equation for aluminum. Fortunately, however, this is no longer necessary since data are now available from which a thoroughly accurate and reliable free energy equation may be derived. The new data will be discussed in the following section.

Experimental Study of Aluminum in Liquid Iron

A few years ago, in attempting to calculate the "deoxidation constant" for aluminum, which is the equilibrium constant for the reaction of aluminum with iron oxide in liquid iron, it was found that all of the necessary data were available except the free energy of solution of aluminum in iron. The use of Equation 20 would be only a rough approximation in this case because the solution of aluminum in iron is not an ideal solution. The following experiments, which were designed to determine directly the free energy of aluminum in liquid iron, form a part of a more comprehensive study of the ternary system, iron-aluminum-silver, in which L. A. Delp is collaborating.

Liquid iron and liquid silver are practically immiscible, separating into two layers like oil and water. Aluminum is quite soluble in both metals and when the three are present together it distributes itself between the other two in accordance with the well known distribution law. Now, the solution of aluminum in liquid silver is approximately an ideal solution, a conclusion which we may draw from the similarity of atomic dimensions and internal pressures of the two metals and their high degree of mutual solubility.

The activity of aluminum in liquid silver may therefore be assumed equal to its mol fraction without probability of any large error, and if its distribution ratio between silver and iron is known, its activity in the latter is determined.

The experiments were carried out in a small closed induction furnace. Electrolytic iron and pure grades of aluminum and silver were melted together, held at 1600 degrees Cent. for thirty minutes,

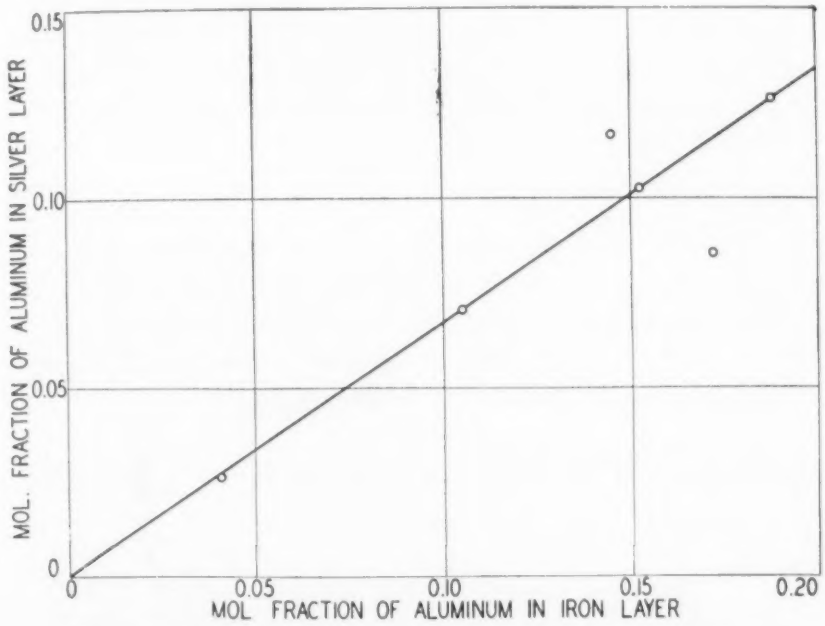

Fig. 13—Distribution of Aluminum Between Liquid Iron and Silver.

then cooled in the furnace. It was impossible to carry out these experiments in air on account of the rapid oxidation of the metal. The use of vacuum was equally impossible on account of the volatility of silver. Attempts to use nitrogen and hydrogen produced very porous ingots from which it was impossible to obtain representative samples. It was therefore necessary to use one of the rare gases and we are indebted to the Bureau of Mines for supplying the helium in which the melts were made.

The solidified metal was found to be clearly separated into two layers, the upper layer rich in iron, the lower rich in silver. Both layers were sampled and analyzed. Results obtained to date show that the ratio of aluminum in the iron layer to aluminum in the silver layer is constant up to 9.9 per cent aluminum in the iron layer and 2.3 per cent in the silver layer. The mol fractions of aluminum in

the two layers are shown in Fig. 13. The straight line indicates a constant distribution ratio, $N'/N = 0.68$, where N is the mol fraction of aluminum in the iron layer and N′ in the silver layer.

If we let c be some small percentage of aluminum in the iron layer, the corresponding mol fraction is $0.5584\ c/27 = 0.0207\ c$. Then at unit concentration in the iron layer the mol fraction of aluminum is 0.0207. Its activity, however, relative to pure liquid aluminum, is equal to its mol fraction in the silver layer which is $0.0207 \times 0.68 = 0.014$. The change in free energy in transferring a mol of aluminum from the pure liquid to the dilute solution in liquid iron in which the concentration of aluminum is one per cent, is 4.575 T log 0.014, hence

$$Al(1) = Al(\%\text{ in Fe});\ \Delta F^\circ = -8.47\ T \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (28)$$

In a later section this equation will be combined with others to calculate the degree of deoxidation obtainable with aluminum. It is of interest to note that if we had used Equation 18 we would have found $\Delta F^\circ = -7.70\ T$, which would have introduced an error of only about 1400 calories at 1600 degrees Cent.

Behavior of Manganese and its Oxide in Liquid Steel and Slag

In order to establish the free energy of manganese oxide from the available data at low or moderately high temperatures, we should require accurate data on the entropy and heat capacity of metal and oxide and on the heat of formation of the latter. The entropy data are available, but published information on heat capacities is scarce and conflicting. Moreover, there is an uncertainty of several thousand calories in the heat of formation of the oxide, and it is mainly for this reason that the calculation of its free energy from low-temperature data will not be attempted.

Fortunately, there are numerous sets of data at high temperatures on the "manganese reaction" which involves the equilibrium between iron, manganese, and their oxides in the liquid state. These data are fairly concordant and their average may be accepted with confidence. The reaction and its equilibrium constant are:

$$FeO\ (\text{in slag}) + Mn(\%\text{ in Fe}) = MnO\ (\text{in slag}) + Fe$$

$$K_{Mn} = \frac{(MnO) \times (Fe)}{(FeO) \times (\%\ Mn)}$$

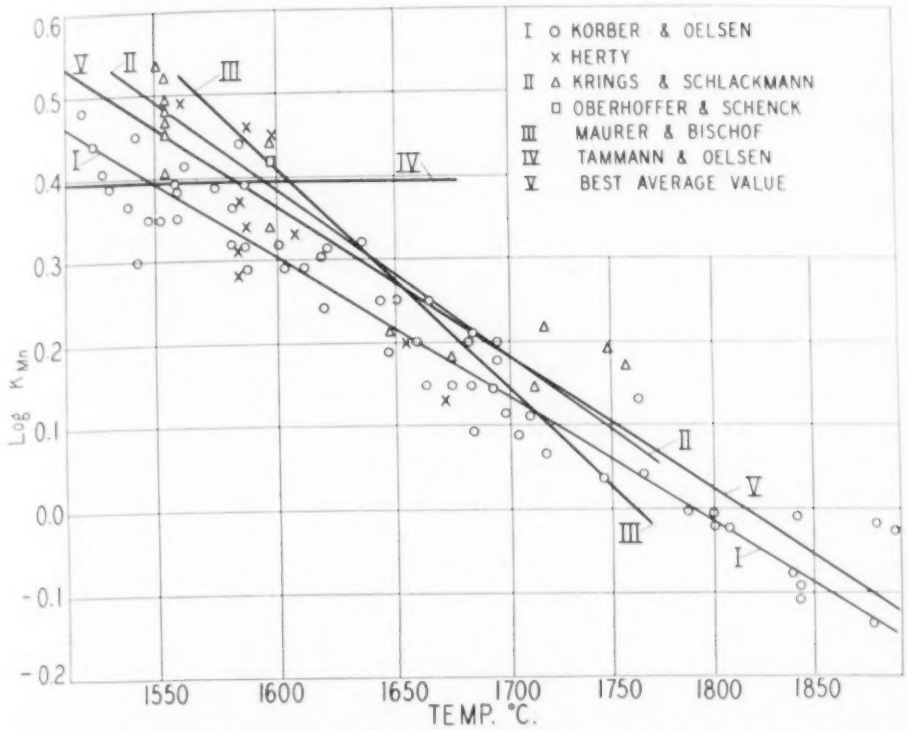

Fig. 14—Manganese Equilibrium Constant K_{Mn} = (MnO) . [Fe]/(FeO) . [% Mn].

This equilibrium has been studied in the open-hearth by von Seth, (45) Colclough,(46) Herty,(47) Styri,(2) Schenck,(48) Oishi,(49) and by Maurer and Bischof.(50) In addition, it has been subjected to exhaustive laboratory investigation by Oberhoffer and Schenck, (51) Körber and Oelsen,(52) and by Krings and Schackmann,(53) The theoretical discussion of this important equilibrium by Tammann and Oelsen(54) failed to recognize the effect of temperature upon the equilibrium. The work of Maurer and Bischof, which has been so extensively published in the European technical press, appears to draw more conclusions than their data could possibly justify. The graphs which they recently published in *Metal Progress* are therefore to be accepted only with extreme caution.

The equilibrium data on the manganese reaction are shown in Fig. 14. The points shown represent the available laboratory data, as well as a number of points taken from open-hearth studies in which the slag was very strongly basic. Curves I and II are the lines drawn by Körber and Oelsen and by Krings and Schackmann, respectively, to represent their experimental results. Curve III which

is due to Maurer and Bischof, is drawn through the average results of Oberhoffer and Schenck at 1600 degrees Cent. Its slope was based upon an erroneous calculation which was not supported by their experimental data. As an average of the available data, Curve V appears to lie within the limits of probable error of all of the investigations, and its slope corresponds with the heat of reaction as closely as this quantity is known. The agreement between the laboratory data involving only the oxides of iron and manganese and the open-hearth data in which these oxides are dissolved in strongly basic slags illustrates the direct applicability of laboratory results to open-hearth practice. It indicates, moreover, that this particular slag-metal reaction attains a state of equilibrium in the open-hearth and, indeed, that the reaction remains at equilibrium during the greater part of the heat. The equation for Curve V is:

$$\text{Log } K = 6600/T - 3.16$$

The change in free energy in the reaction is then given by the equation:

$$\text{FeO(l)} + \text{Mn(\% in Fe)} = \text{MnO(l)} + \text{Fe(l)};$$
$$\Delta F^\circ = -30{,}200 + 14.46T \quad \ldots\ldots (29)$$

The free energy of liquid manganese oxide formed from gaseous oxygen and dissolved manganese in liquid steel is found by combining (11) and (29):

$$\text{Mn(\% in Fe)} + \tfrac{1}{2}\,O_2 = \text{MnO(l)};\ \Delta F^\circ = -76{,}580 + 21.06\ T \quad \ldots (30)$$

When iron oxide is added to a bath containing manganese or, conversely, when manganese is added to a bath containing dissolved iron oxide, liquid nonmetallic inclusions are formed. These inclusions consist of a solution of MnO and FeO, which, according to the work of Herty and Daniloff, are miscible in all proportions. The reaction and its free energy are found by combining Equations (8) and (30):

$$\text{FeO(\% in Fe)} + \text{Mn(\% in Fe)} = \text{Fe(l)} + \text{MnO(l)};\ \Delta F^\circ =$$
$$-44{,}800 + 22.22\ T \quad \ldots\ldots (31)$$

By means of Equations 29 and 31 we are enabled to predict not only the composition of the MnO-FeO inclusions formed as indicated above, but also the percentage of oxygen which remains in the

bath as dissolved FeO. The ratio of manganese oxide to ferrous oxide in the inclusions as calculated from Equation 29 or Fig. 14 is shown as a function of the manganese content of the metal in Fig. 15. It should be remembered that these curves will not agree precisely with any one of the several sets of data but rather represent the average of all data available at the present time.

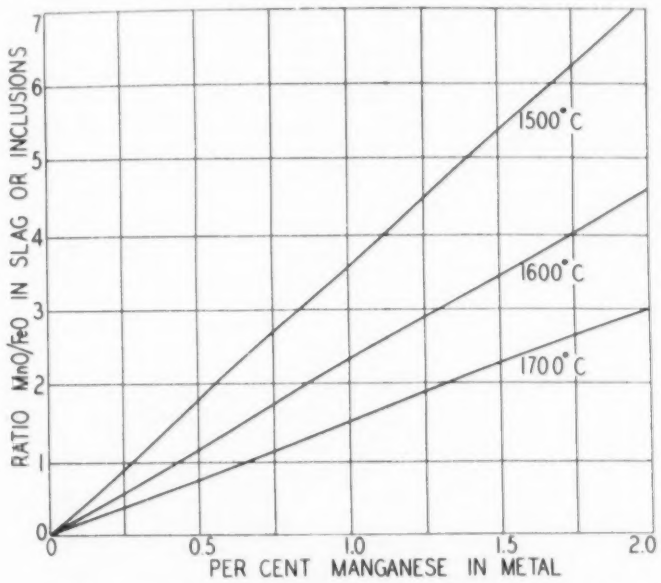

Fig. 15—Relation Between Composition of Metal and of Basic Nonmetallic Phase.

When manganese alone is used as a deoxidizer the relationship between the manganese content of the bath and its maximum dissolved ferrous oxide is given by the following equilibrium which is obtained from Equation 31.

$$K = \frac{(MnO)}{(\%\ FeO\ in\ Fe)\ (Mn\ \%)};\quad \log K = 9790/T - 4.86$$

From this we find that at 1500, 1600 and 1700 degrees Cent., respectively, the values of K are 4.55, 2.30, and 1.25. Now, from Fig. 15, we can obtain the per cent of MnO in the inclusions that are formed (the balance being FeO) and therefore for any given manganese content of the bath we can obtain, by means of the above constant, the limiting percentage of oxygen present as dissolved FeO. Since other oxides are much less soluble than FeO, this will represent essentially the maximum dissolved oxygen. The calculation

is shown for 1600 degrees Cent. in Table 7. The mol fraction of MnO was computed from Fig. 15, and the conversion from activity of FeO to per cent oxygen was made by means of Fig. 6. The results of similar calculations at 1500 and 1700 degrees Cent. are included in Fig. 16. They show quite clearly that manganese alone is

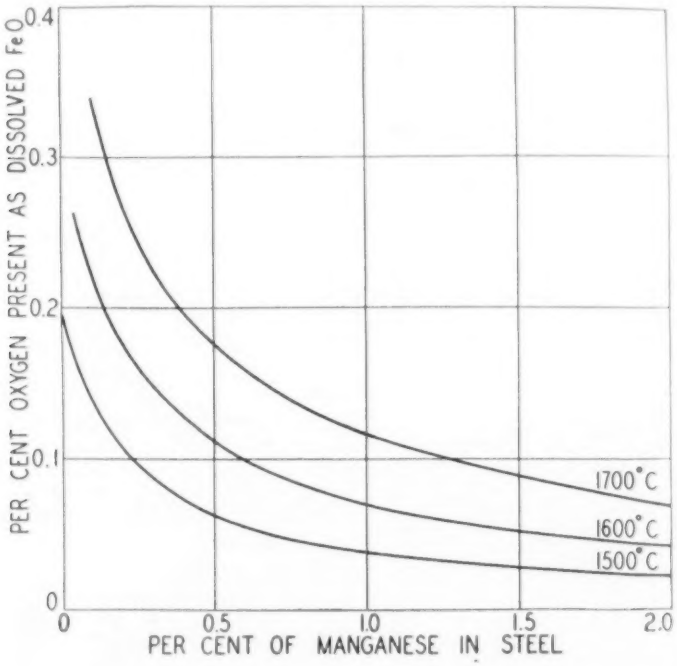

Fig. 16—Deoxidation Diagram for Manganese.

a very poor deoxidizer, for even with one per cent manganese in the bath the dissolved oxygen may be as high as 0.07 per cent at 1600 degrees Cent. The curves of Fig. 16 are very different from a similar curve published by Oberhoffer and H. Schenck. They are, however, in qualitative agreement with Körber's deoxidation diagram.

Table VII
Equilibrium in the Deoxidation of Steel With Manganese at 1600 Degrees Cent.

Manganese in Metal (Per cent)	MnO in Inclusions (Mol fraction)	FeO in Metal (Activity)	Oxygen in Metal (Per cent)
0.05	0.103	0.90	0.25
0.10	0.186	0.81	0.22
0.20	0.315	0.69	0.17
0.50	0.535	0.47	0.11
1.00	0.696	0.30	0.07
2.00	0.821	0.18	0.04

The foregoing discussions and computations are applicable only so long as the nonmetallic phase, inclusions or slag, is definitely basic. In the acid process another factor enters in, due to the fact that manganous silicate is more stable than ferrous silicate, and the equilibrium constant as ordinarily stated in terms of mol fraction becomes definitely larger than in basic slags. No laboratory data on acid

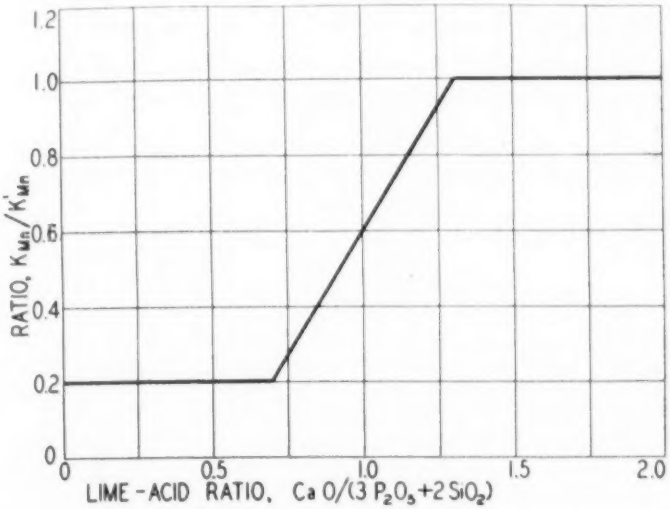

Fig. 17—Variation of Manganese Equilibrium with Basicity of Slag.

slags are available, but in a recent unpublished review of the data on acid and basic open-hearth slags L. H. Gaston has reached some interesting conclusions. He expresses the basicity of the slag as the ratio of the total number of mols of lime to three times the number of mols of phosphoric acid, plus twice the number of mols of silica. This results from the hypothesis that the stable compounds in basic slag are 3 $CaO.P_2O_5$ and 2 $CaO.SiO_2$. The lime-acid ratio is therefore

$$(CaO)/[3(P_2O_5) + 2(SiO_2)].$$

Let us define an apparent manganese constant by the formula

$$K'_{mn} = \frac{(\%\ MnO)}{(\%\ FeO)\ (\%\ Mn)}$$

In strongly basic slags it is found that K_{mn} is numerically equal to K'_{mn}. In acid slags K'_{mn} becomes much larger. The ratio K_{mn}/K'_{mn} is plotted against the lime-acid ratio in Fig. 17, which is based

upon data of Schenck,(48) Herty,(47) Styri,(2) and Oishi.(49) In making the plot, only those points were used for which direct determinations of temperature were available, and in which no additions had been made to the bath within the previous twenty minutes. Slags in which the lime-acid ratio lies between 0.7 and 1.3 are to be classified as intermediate. In the acid slags below 0.7 the value of K'_{mn} is approximately five times as large as K_{mn}, and from this we conclude that the ferrous silicates are five times as highly dissociated into their component oxides as are the corresponding manganous silicates. The thermodynamic treatment of acid slags or silicate inclusions will not be possible until we have experimental data on the activities of their components or upon their degree of dissociation.

Deoxidation with Silicon

The stable form of silica at high temperatures is cristobalite, and we shall therefore confine our calculations to this form. The entropies of silicon, oxygen and cristobalite according to Kelley(8) are, respectively, 4.5, 49.0, and 10.4 units at 25 degrees Cent. The heat of formation of cristobalite from Roth's(55) data is $\Delta H = -205{,}600$ calories. The free energy at 25 degrees Cent. is, by Equation III, $\Delta F^\circ_{298} = -192{,}750$ cal. To bring these data up to steel-making temperatures requires the heat capacities of all three substances. Taking that of oxygen from the recent work of Lewis and von Elbe(57) and those of silicon and silica from Kelley's compilation, we find at the melting point of silicon (1638°K.):

$$\Delta H = -203{,}000 \text{ and } \Delta S = -40.2.$$

From the data of Haughton and Becker, the heat of fusion of silicon, calculated from the effect of the partially dissociated FeSi upon its melting point, is 10,000 calories. The change in free energy attending the fusion of silicon is therefore 10,000 — 5.95 T. Subtracting this from the above data we obtain the equation:

$$Si(l) + O_2 = SiO_2(\text{crist.}); \Delta F^\circ = -213{,}000 + 46.15\ T \ldots\ldots (32)$$

When steel is deoxidized with silicon a variety of inclusion types are formed containing variable proportions of FeO and SiO_2. When the dissolved free silicon in the bath, after the deoxidation reaction has ceased, amounts to more than 0.03 per cent, then, according to Herty's(58) observations, the inclusions are of the glassy

type very high in silica. We can calculate the equilibrium constant for the reaction by which these inclusions are formed and thus find the limiting conditions in the deoxidation with silicon. The activity of SiO_2 in the glassy silicates is not very different from the activity of cristobalite, so that the use of the free energy of the latter will

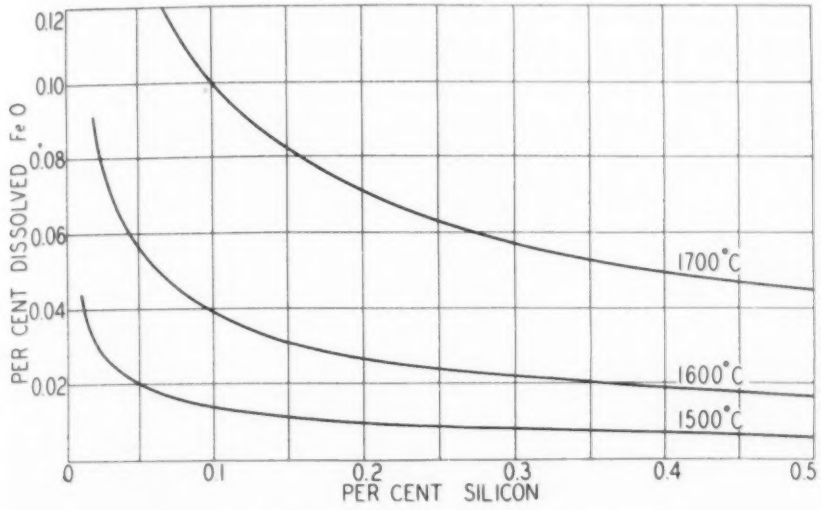

Fig. 18—Deoxidation Diagram for Silicon in Steel.

not introduce an appreciable error. The combination of Equations 32, 8, and 27 leads to the following result:

$$2\ FeO(\%\ in\ Fe) + Si(\%\ in\ Fe) = 2\ Fe(l) + SiO_2\ (crist)$$
$$\Delta F^\circ = -142{,}440 + 56.25\ T \qquad (33a)$$

When Equation 33a is solved for the equilibrium constant at 1600 degrees Cent., it is found that,

$$(\text{per cent FeO})^2 \times (\text{per cent Si}) = 0.48 \times 10^{-4}.$$

This is somewhat smaller than Herty's values, 1.49 to 1.65×10^{-4}, and in view of the uncertainties involved in Equation 27 the experimental result is probably more accurate than the calculated. The free energy equation may be re-written to conform to the experimental value at 1600 degrees Cent. but retaining the calculated temperature coefficient:

$$2\ FeO(\%\ in\ Fe) + Si(\%\ in\ Fe) + 2\ Fe(l) + SiO_2\ (inclusions)$$
$$\Delta F^\circ = -138{,}000 + 56.25\ T. \qquad (33b)$$

The equilibrium constants, (per cent FeO)^2 × (per cent Si), calculated from 33b at 1500, 1600 and 1700 degrees Cent. are, re-

spectively, 1.9×10^{-5}, 1.5×10^{-4} and 1.0×10^{-3}. From these constants the maximum dissolved FeO after deoxidation with silicon has been calculated and the results are shown in Fig. 18. It should be emphasized that the per cent silicon shown in the figure is not the amount added to the bath, but the amount which remains after the reaction is finished and exclusive of that present as SiO_2.

Deoxidation with Aluminum

When aluminum is added to liquid steel the main reaction is

$$2\ Al + 3\ FeO\ (in\ Fe) = Al_2O_3 + 3\ Fe(l)$$

The deoxidizing power of aluminum is known to be very great, but it is not enough to remove every trace of dissolved ferrous oxide. Attempts to determine the residual dissolved FeO in equilibrium with a given percentage of metallic aluminum have not heretofore met with conspicuous success. It is now possible to obtain the answer to this long-standing problem by the aid of thermodynamics with greater precision than one could hope to obtain in a direct experimental manner.

The heat of formation of aluminum oxide, according to Roth, (55) is $\Delta H = -380{,}800$ calories. The entropy change(8) is -74.45 calories at 25 degrees Cent. and therefore the free energy at 25 degrees Cent. is given by the exprssion:

$$2\ Al\ (s) + 3/2\ O_2\ (g) = Al_2O_3\ (s);\ \Delta F^\circ_{298} = -358{,}600$$

The data needed to compute the change in this value in going from 25 to 1600 degrees Cent. are all available. The heat capacity of solid and liquid aluminum and its heat of fusion are taken from Kelley's bulletin.(9) The data on heat capacity of Al_2O_3 are shown in Fig. 19, which, incidentally, is a nice example of almost exact agreement among five independent researches in as many different laboratories. The curve is given by the formula, $C_p = 26.0 + 0.0034\ T - 704{,}000\ T^{-2}$, which is used along with the other data mentioned to find the following equation which is valid at the temperatures of liquid steel.

$$2\ Al(l) + 3/2\ O_2 = Al_2O_3\ (s);\ \Delta F^\circ = -382{,}100 + 77.20\ T \ldots (34)$$

Now, in the case of aluminum, the free energy of solution of the liquid metal in liquid iron is known from the experimental work on the iron-aluminum-silver system and is given in Equation 28. By

combining Equations 8, 28, and 34, we find the free energy of deoxidation of steel with aluminum:

$$3\ FeO(\%\ in\ Fe) + 2\ Al(\%\ in\ Fe) = Al_2O_3\ (s) + 3\ Fe\ (l)$$
$$\Delta F^\circ = -286{,}760 + 97.62\ T \qquad (35)$$

This equation is based entirely upon experimental data, although of a very indirect nature, and since all of the data appear to be reliable,

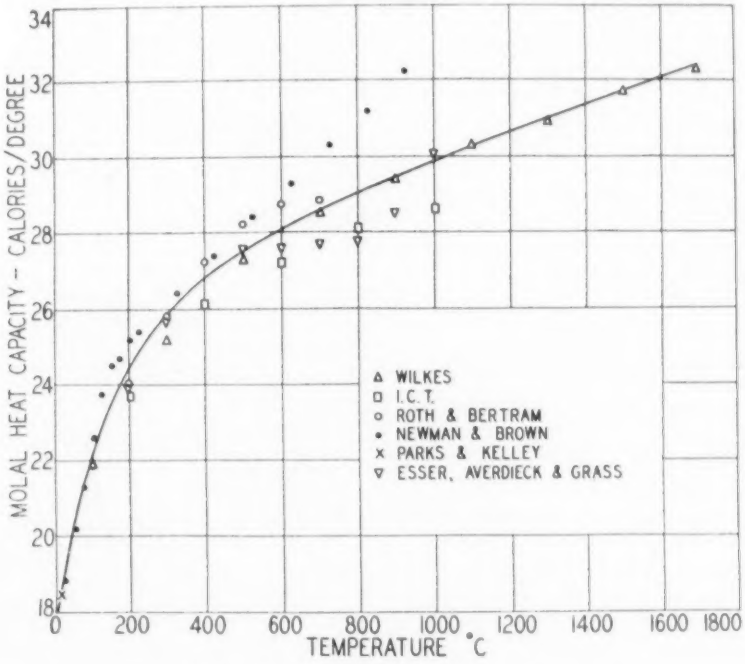

Fig. 19—Heat Capacity of Al_2O_3.

there is no reason to suspect that it contains any unduly large error.

The equilibrium constant obtained directly from Equation 35 is

$$K = \frac{1}{(\%\ FeO)^3 \times (\%\ Al)^2};\ \log K = 62{,}700/T - 21.35$$

The values of $\frac{1}{K} = (\text{per cent FeO})^3 \times (\text{per cent Al})^2$ at 1500, 1600, and 1700 degrees Cent. are, respectively, 1×10^{-14}, 7×10^{-13}, and 4×10^{-11}. From these constants are calculated the per cent of dissolved FeO in the presence of given percentages of residual metallic aluminum dissolved in the bath. The results of the calculations are shown in Fig. 20.

The constants are of an altogether different order of magnitude

from that found by Herty, Fitterer and Byrns(59) at 1600 degrees Cent. which was 5.7×10^{-7}. The calculated percentage of dissolved oxygen is very much lower than their results would indicate, since their curve passes above the upper right-hand corner of Fig. 20. It was Herty's contention that aluminum is not a more powerful deoxidizer than silicon. The present calculations show that it is

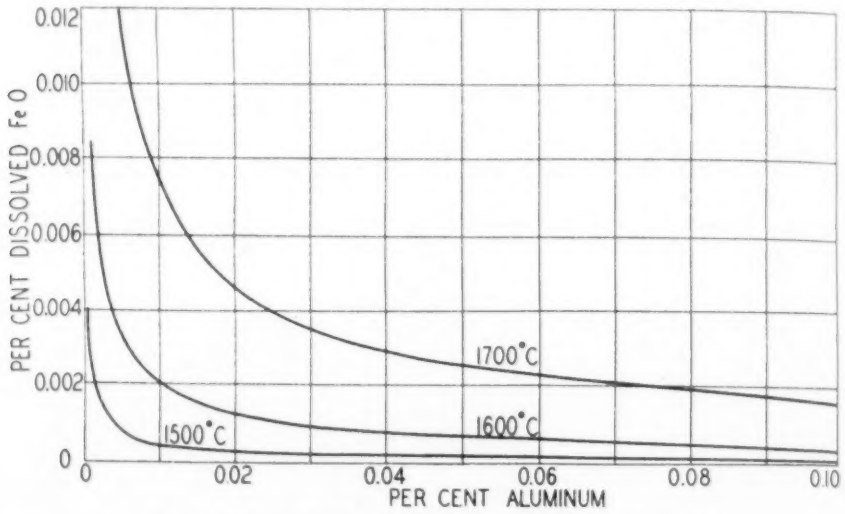

Fig. 20—Deoxidation Diagram for Aluminum in Steel.

much more powerful than silicon and that even with only a few thousandths of one per cent aluminum present as such in the bath, the dissolved ferrous oxide is reduced to an exceedingly low percentage.

There can be little doubt but that aluminum is a more complete deoxidizer than was indicated by Herty's results. The extreme difficulties of the experimental method are quite apparent and it is doubtful if the deoxidation constant of this reaction can ever be directly determined. Considerable support is given to the contention that aluminum is an exceedingly complete deoxidizer, by the author's experience in the determination of the total oxygen content of steels treated in the ladle with 0.05 per cent aluminum and containing a residual of perhaps 0.01 or 0.02 per cent. It has been observed repeatedly that if such steels are clean, that is to say, comparatively free from inclusions, their total oxygen content is often below 0.002 per cent, occasionally 0.001. Allowing for the small amount of oxygen always present as alumina inclusions in such steels the oxygen present as dissolved FeO must be exceedingly minute.

If Herty's constant were correct, an addition of 0.05 per cent aluminum, even if the recovery were 100 per cent, would not reduce the oxygen content below 0.01 per cent.

The curves of Fig. 20 serve to emphasize the enormous difference between an aluminum-treated steel which contains no residual free aluminum; that is to say, where all the added aluminum is used up in the reaction, and one in which even a small amount, say 0.01 per cent, is retained as free aluminum. In the former case there is absolutely no guarantee of efficient deoxidation, while in the latter the ferrous oxide will be below 0.002 per cent. Here is a case where 0.01 per cent of a metal may exert a very profound though indirect effect upon the properties of the steel.

Formation of Chromic Oxide in Steel

When ferrochrome is added to the steel bath, does a reaction occur between the chromium and the dissolved ferrous oxide? If so, how well must the bath be deoxidized before the chrome addition to avoid loss of chromium? Is chromium itself a deoxidizer? Thermodynamic data are available from which answers may be obtained.

Von Wartenberg and Aoyama(60) measured the equilibrium in the reaction of metallic chromium with water vapor forming hydrogen and chromic oxide. The results of their experiments at the two highest temperatures employed, 1133 and 1380 degrees Cent., are expressed by the following equation:

$$2\ Cr + 3\ H_2O = Cr_2O_3 + 3\ H_2;\ \Delta F^\circ = -93{,}900 + 26.1\ T \ldots\ldots (36)$$

When Equation 2 for the free energy of water vapor is multiplied by 3 and added to the above, we obtain:

$$2\ Cr + 3/2\ O_2 = Cr_2O_3;\ \Delta F^\circ = -274{,}440 + 67.62\ T \ldots\ldots\ldots (37)$$

To find the free energy change for the reaction of chromium dissolved in steel with dissolved ferrous oxide, it is necessary to combine Equation 37 with Equations 8 and 25, which gives:

$$3\ FeO(\text{in Fe}) + 2\ Cr(\text{per cent in Fe}) = 3\ Fe(l) + Cr_2O_3\ (s);$$
$$\Delta F^\circ = -187{,}800 + 93.32\ T \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (38)$$

The equilibrium constant corresponding to this reaction is $\log K = 41{,}050/T - 20.40$. From this the following values of $(\text{per cent } FeO)^3 \times (\text{per cent } Cr)^2$ are found. At respectively 1500, 1600, and 1700 degrees Cent. the constant is 0.0016, 0.031, and 0.40. From these constants the graphs of Fig. 21 have been constructed, show-

ing the per cent FeO in equilibrium with a given percentage of chromium in the presence of chromic oxide.

These graphs demonstrate very clearly a number of points in regard to the addition of chrome to the bath and provide the answer to some of the questions that have arisen regarding the behavior of

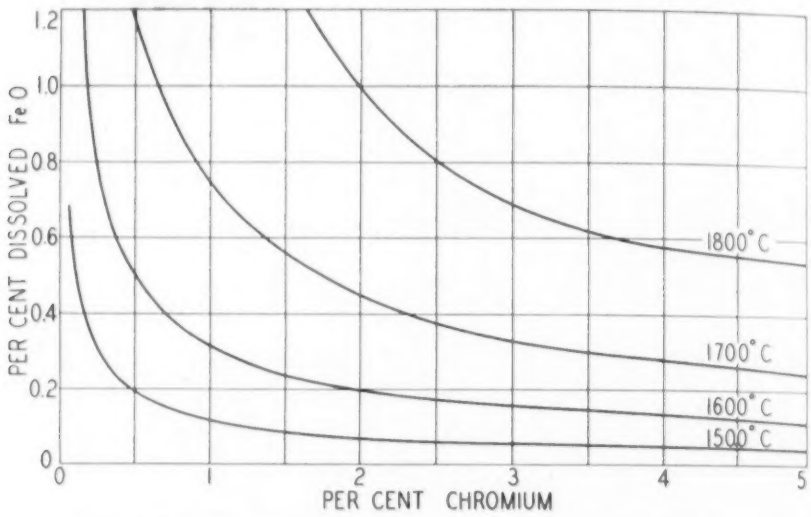

Fig. 21—Relation Between Dissolved FeO and Chromium in Steel.

this element. If the bath is high in oxygen, a reaction occurs when chromium is added, giving rise to the familiar chrome inclusions. The lower the temperature, the lower must be the ferrous oxide of the bath if the formation of these inclusions or loss of chromium is to be avoided. At high temperatures there is virtually no reaction between chromium and oxygen in the bath so that moderate amounts of the two may be present simultaneously without reaction occurring. Conversely, if it is desired to remove chromium from the bath the temperature must be as low as possible. It should be noted, however, that Equation 38 and Fig. 21 do not apply to chrome which is present in the slag, although the conclusions regarding the influence of temperature are doubtless correct in this case also. The treatment of the subject of chromic oxide in slags awaits further knowledge as to the free energy of such compounds as $FeO.Cr_2O_3$.

An Estimate of the Deoxidizing Powers of Titanium, Zirconium, and Vanadium

Titanium and zirconium are used occasionally as deoxidizers, and an estimate of their deoxidizing powers will therefore be of in-

terest. Sufficient data for an exact calculation are not available, but by using the equation for deoxidation with silicon as a basis for comparison we can reach an estimate of the deoxidation constants for these two elements which will be as good an approximation as can be obtained at the present time.

The equation for deoxidation with silicon was:

$$2\,FeO(\%\text{ in Fe}) + Si(\%\text{ in Fe}) = 2\,Fe(l) + SiO_2\ (\text{inclusions});$$
$$\Delta F^\circ = -138{,}000 + 56.25\,T \qquad (33b)$$

Comparison with Equation V shows that this is made up of a heat term, —138,000 calories, and an entropy term, —56.25. The corresponding heat terms for titanium and zirconium will be assumed to differ from that of silicon only as the heats of formation of their oxides differ. The entropy terms will differ only as regards the effect of atomic weight upon Equation 20. The comparison of the three elements is shown in Table VIII. The second column gives the heat of formation of the oxide at room temperature, according to Roth and Becker (56); the third column gives the difference between the other elements and silicon. In the fourth column the term for silicon comes from Equation 33b and the others are found by adding to this the differences of the third column. A similar scheme is used to estimate the entropy terms of the last column, that for silicon being the last term of Equation 33b.

The following approximate equations for the free energy of deoxidation of steel by these elements are obtained directly from Table VIII.

$$2\,FeO(\%\text{ in Fe}) + Ti(\%\text{ in Fe}) = 2\,Fe(l) + TiO_2$$
$$\Delta F^\circ = -151{,}000 + 57.3\,T \qquad (39)$$
$$2\,FeO(\%\text{ in Fe}) + Zr(\%\text{ in Fe}) = 2\,Fe(l) + ZrO_2$$
$$\Delta F^\circ = -190{,}000 + 58.6\,T \qquad (40)$$

Table VIII
Comparison of Constants for Silicon, Titanium and Zirconium

Element	Heat of Formation of Oxide Kilo-cal.	Difference from Silicon	Heat of Reaction with FeO Kilo-cal.	Δ S Eq. 20	Difference from Silicon	Reaction with FeO Δ S
Si	—206	0	—138	7.78	...	—56.25
Ti	—219	—13	—151	8.85	1.07	—57.3
Zr	—258	—52	—190	10.13	2.35	—58.6

The corresponding expressions for the equilibrium constants of the reactions are:

$$K_{Ti} = (\%\ FeO)^2\ (\%\ Ti);\ \log K = -33{,}000/T + 12.52$$
$$K_{Zr} = (\%\ FeO)^2\ (\%\ Zr);\ \log K = -41{,}500/T + 12.81$$

The values of the two constants at 1600 degrees Cent. are, for titanium 8×10^{-6}, and for zirconium 5×10^{-10}. These values are to be considered only approximately valid as to order of magnitude. The significance of these constants in terms of deoxidizing power will be more evident later when the residual ferrous oxide after addition of various deoxidizers is compared graphically. It is quite evident that titanium is a somewhat more powerful deoxidizer than silicon, while zirconium is much more powerful. These conclusions are in complete agreement with results of the careful experimental investigations of Becket (61) and the recent work of Zieler (62).

In a very similar manner, the deoxidizing power of vanadium may be roughly estimated. There are a number of oxides of vanadium, but in the reaction of this metal with iron oxide the most complete deoxidation is accompanied by the formation of the spinel FeV_2O_4 found by Mathewson, Spire, and Samans (63). Thermodynamic data on spinels are conspicuous by their absence, but it seems probable that the free energy change in the formation of the spinel from its component oxides, in this case FeO and V_2O_3, is relatively small. Accordingly, we shall estimate the free energy of V_2O_3 and use this as a first approximation in fixing the deoxidizing power of vanadium.

For the heat of the reaction the International Critical Tables give:

$$2\ V(s) + 3/2\ O_2 = V_2O_3(s);\ \Delta H = -350{,}000\ \text{cal.}$$

From computations on the similar reactions involving aluminum and chromium it is found that the heat of reaction at high temperatures is about 4000 calories less than at room temperature. Similarly, the entropy terms in the reactions of aluminum and chromium are not far apart and their average will be used for vanadium. Thus, we find as an approximation

$$2\ V(s) + 3/2\ O_2 = V_2O_3(s);\ \Delta F^\circ = -346{,}000 + 71.0\ T \ldots\ldots (41)$$

When this is combined with Equations 8 and 26 the result is

$$3\ FeO(\%\ \text{in Fe}) + 2\ V(\%) = 3\ Fe(1) + V_2O_3(s);$$
$$\Delta F^\circ = -259{,}060 + 96.62\ T \ldots\ldots\ldots\ldots\ldots (42)$$

The equilibrium constant of this reaction at 1600 degrees Cent. is found to be

$$K_V = (\text{per cent FeO})^3 \times (\text{per cent V})^2 = 8 \times 10^{-10}$$

from which it is seen that vanadium has distinctly less deoxidizing power than has aluminum. The comparison with other elements will be made later.

Deoxidation with Sodium, Magnesium and Calcium

Numerous attempts have been made to use sodium, magnesium, and calcium as deoxidizers and we occasionally hear extravagant claims of absolutely complete deoxidation with one of these elements. Sufficient data are available for an accurate calculation of the deoxidizing powers of calcium and magnesium and the results will show that both are powerful deoxidizers. Concerning sodium, attention is called to the fact that Fox and White(64) were able to reduce sodium carbonate to metallic sodium with carbon at 1000 degrees Cent. and atmospheric pressure. This does not indicate a high degree of stability for the oxide and its stability decreases with rising temperature. Moreover, at the temperature of liquid steel sodium has a vapor pressure of about 60 atmospheres. The violent reaction which has been observed by Zieler(62) and by every other investigator, including the writer, who has added sodium to liquid steel is simply the vaporization of the metal carrying with it more or less of the bath. On both theoretical and experimental grounds, Zieler is correct in stating that sodium is not suitable for use in the deoxidation of steel.

The free energy of the oxides of magnesium and calcium are obtained from the following data. The entropies of the metals and their oxides are given by Kelley.(8) The heat capacities and heats of fusion are taken from Kelley's forthcoming bulletin,(9) with the exception of the data for calcium oxide, for which the following equation, based upon data of the International Critical Tables and of Esser, Averdieck, and Grass (65), is to be preferred:

$$CaO;\ C_P = 9.72 + 0.00242\ T - 38{,}400\ T^{-2}$$

The heats of formation of the two oxides are given by the International Critical Tables. Since both of these metals are gases at steel-making temperatures, we require their vapor pressures and

heats of vaporization. These data are obtained from the work of Hartmann and Schneider (66). Without going into further details of the calculations, the results are presented in the following equations which are applicable at the temperatures of the steel bath.

$$Mg(g) + \tfrac{1}{2} O_2 = MgO(s);\ \Delta F^\circ = -176{,}500 + 47.5\ T \quad \ldots\ldots (43)$$
$$Ca(g) + \tfrac{1}{2} O_2 = CaO(s);\ \Delta F^\circ = -192{,}000 + 49.1\ T \quad \ldots\ldots (44)$$

These expressions may be combined with Equation 8 to obtain the free energy change in the deoxidation of liquid steel by the two gaseous metals:

$$FeO(\%\text{ in Fe}) + Mg\ (g) = Fe(1) + MgO(s);$$
$$\Delta F^\circ = -144{,}720 + 48.66\ T \quad \ldots\ldots (45)$$
$$FeO(\%\text{ in Fe}) + Ca(g) = Fe(1) + CaO(s);$$
$$\Delta F^\circ = -160{,}220 + 50.26\ T \quad \ldots\ldots (46)$$

These metals are, of course, never added to the steel bath directly as gases, but rather as alloys or compounds such as silicides or borides, from which the gases are evolved upon mixing with the liquid steel. The equilibrium constants obtained from Equations 42 and 43 at 1600 degrees Cent. are:

$$(\%\ FeO)\ (Mg) = 6 \times 10^{-7}$$
$$(\%\ FeO)\ (Ca) = 2 \times 10^{-8}$$

If the pressure of the gaseous metals is one atmosphere, that is, if the bath is saturated with the deoxidizer at atmospheric pressure, then (Mg) or (Ca) becomes equal to one and the constant is equal to the per cent of dissolved FeO. Just what percentage of the metal must be present to obtain this high degree of deoxidation is not known, but it will correspond to the solubility of the metal in liquid iron, which is probably small.

Discussion and Summary

The results of the calculations on the deoxidation of steel at 1600 degrees Cent. are summarized in Fig. 22, which shows the percentage of dissolved FeO as a function of the percentage of the alloy remaining after the deoxidation reaction is complete. The lines representing manganese and silicon are based upon direct experimental data, those for chromium, aluminum, magnesium and calcium are based also upon complete experimental data, though of a very indirect nature. The lines for titanium, vanadium and zirconium are estimates which may be very considerably in error. It seems reasonable to suppose that they are given in their correct order

and that all three lie between silicon and aluminum. In the development of this diagram, the effects of further reactions upon the deoxidation products have been omitted from consideration, as have also the effects of the simultaneous addition of two or more de-

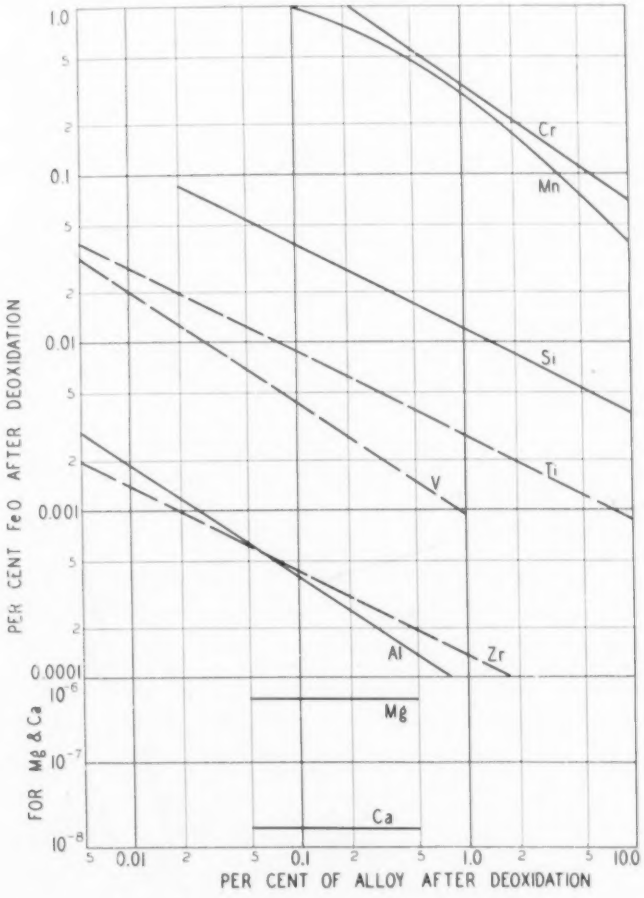

Fig. 22—Comparison of Deoxidizing Powers.

oxidizers. Either of these effects would tend to increase the degree of deoxidation attainable with a given alloy.

Considerable caution should be exercised in the interpretation of the extremely high degrees of deoxidation indicated for calcium and magnesium. It is very doubtful if any such deoxidation could be obtained in practice, for the reason that any bath so low in FeO would have a very strong tendency to pick up oxygen from anything with which it happened to be in contact, such as furnace bottom, ladle brick, and even from the deoxidizing carbide slag of an electric furnace. There is, moreover, the distinct possibility that many of the

Table IX

Standard Free Energies of Formation at 1600 Degrees Cent.

Substance	Reference State	$\Delta F°_{1873}$	Equation
H_2, O_2, Mg, Ca	gas, 1 atm.	0	def.
H_2O	gas, 1 atm.	−34,260	1 and 2
CO	gas, 1 atm.	−65,870	5
CO_2	gas, 1 atm.	−94,950	6
Fe	liquid	0	def.
FeO	activity = 1 (1% in Fe)	−33,950	8
FeO	liquid	−34,020	11*
C	graphite	0	def.
C	1% in Fe	−12,340	18*
Mn, Ni, Si, Al	liquid	0	def.
Mn	1% in Fe	−17,060	21
Ni	1% in Fe	−17,250	22
Si	1% in Fe	−21,570	27*
Al	1% in Fe	−15,860	28
Cr, V, Ti, Zr	solid	0	def.
Cr	1% in Fe	−16,460	25
V	1% in Fe	−16,530	26
MnO	liquid	−54,200	21 and 30*
SiO_2	cristobalite	−126,560	32
Al_2O_3	solid	−237,500	34
Cr_2O_3	solid	−147,790	37
TiO_2	solid	.....	39*
ZrO_2	solid	.....	40*
V_2O_3	solid	−213,020	41*
MgO	solid	− 87,530	43
CaO	solid	−100,040	44

products of deoxidation are themselves soluble in liquid iron to some extent. The contribution of this solubility to the total dissolved oxygen of the bath will ordinarily be small, but in the highly deoxidized bath represented by the lower portions of Fig. 22, the dissolved oxides other than FeO may assume a greater importance than has hitherto been accorded them. This thought is in line with the recent paper by Sims and Lillequist(*67*) and it is interesting to note that according to Fig. 18, if we melted absolutely pure iron in a silica crucible in an inert atmosphere, the melt would contain, at equilibrium at 1600 degrees Cent., 0.018 per cent silicon and 0.092 per cent FeO, which is equivalent to 0.02 per cent oxygen. Thus, we would have an apparent solubility of SiO_2 in iron of at least 0.038 per cent.

In conclusion, the calculations of this paper are summarized in a table of standard free energies at 1600 degrees Cent., Table IX. From this table it is possible, with the aid of Equation III, to compute the equilibrium constant for any reaction involving only the substances included in the table. For calculations at temperatures other than 1600 degrees Cent., the original equations should be employed. It must be recognized that some of the data of Table IX are less certain than the others. These data, which are based to some

extent upon estimates or long extrapolations, are indicated by an asterisk attached to the equation number.

Further work is in progress in this laboratory which will not only extend the thermodynamic treatment to include substances other than metals and their oxides, but will also, we hope, improve the accuracy of certain of the data upon which the present calculations are based.

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DISCUSSION

Written Discussion: By H. C. Vacher, assistant scientist, Bureau of Standards, Washington, D. C.

Dr. Chipman has shown by means of thermodynamics how a great mass of apparently unrelated data can be crystallized into a few related equations which describe quantitatively the chemistry of steel making. In a sense he has provided the research worker in steel making with a filing system that will prove a valuable aid in comparing or correlating new data with data already acquired. The Bureau of Standards has recently completed an investigation on the systems liquid iron-carbon oxides and liquid iron-hydrogen and water vapor. This work will be described in a paper in a forthcoming issue of the Journal of Research. The data from this investigation can be compared directly with data represented by Chipman's equations for the following reactions:

$$(7)\ \mathrm{FeO}\ (\%\ \text{in Fe}) + \mathrm{H_2} = \mathrm{Fe}(1) + \mathrm{H_2O}$$
$$(9)\ \mathrm{FeO}\ (\%\ \text{in Fe}) + \mathrm{CO} = \mathrm{Fe}(1) + \mathrm{CO_2}$$

The data obtained at the Bureau indicate that the values of the equilibrium constants for reactions 7 and 9 are 0.855 and 0.209, respectively, at 1580 degrees Cent. The value, 0.855, was obtained at concentrations of ferrous oxide equivalent to oxygen contents of approximately 0.01 per cent and the value 0.209 at oxygen contents of approximately 0.15 per cent. Chipman's equations for

reactions 7 and 9 give values for these constants of 1.16 and 0.295, respectively. These values are not directly comparable as the Bureau's values are based on concentrations of ferrous oxide and Chipman's values are based on the activity of ferrous oxide. However, by the use of Chipman's chart, Fig. 6, the values, 1.16 and 0.295, can be converted to values based on concentrations of ferrous oxide that would be obtained at oxygen contents used in the Bureau's investigation. The values converted to ferrous oxide concentration are 1.16 and 0.264, respectively. The values, 0.855 and 0.209, obtained at the Bureau and the values, 1.16 and 0.264, obtained from Chipman's equations are in good agreement considering the experimental difficulties involved in their determination.

Written Discussion: By J. B. Austin, U. S. Steel Corporation research laboratories, Kearny, N. J.

It has been said that no study of natural phenomena can be called a science until the results can be formulated mathematically, in other words no body of knowledge is really a science until its organization has been perfected to such an extent that it can be expressed in a few brief generalizations. It speaks well, therefore, for recent advances in our knowledge of the deoxidation of steel that the tremendous amount of information which has been gathered on the subject can be put into the brief yet convenient and accessible form given in this paper. The paper also speaks eloquently for Dr. Chipman's ability as a critical surveyor of this field.

While a detailed discussion of such a comprehensive paper is out of the question there are a few points upon which I should like to comment. I note that equation 8 is slightly different from the corresponding one in his paper in the Journal of the American Chemical Society. The difference seems to be due to the use of different data for hydrogen-water vapor equilibrium and I should like to know which equation in his judgment is the more accurate. On page 411 equations are given for the change in free energy accompanying the solution of liquid Mn, Cr and Ni. As I understand the derivation of these equations they apply only to a 1 per cent solution. If this is true it should perhaps be emphasized to avoid confusion since the text says that "these equations are strictly valid only for low concentrations" implying that they hold for percentages other than 1. Finally, I am interested in the demonstration on page 432 that pure liquid iron even in an inert atmosphere will take up silica from a crucible. This result is directly in line with the conclusion which Mr. Pierce and I reached in studying the transformation of pure iron and makes it doubly clear that if one wants very pure iron it must be made by some method which does not involve melting the sample—at least until improved refractories are available.

Written Discussion: By A. B. Kinzel, Union Carbide and Carbon research laboratories, Long Island City, N. Y.

Dr. Chipman is to be congratulated on this excellent exposition of the statics of steel making reactions. The paper is a model of clarity and precision, and the introductory remarks leading up to the conception of activities are more easily understood than similar matter found in most textbooks. The experimental work is so clean-cut and the reasoning in general so syllogistic that there is very little to discuss with respect to the material presented.

However, the facts should be stressed that Dr. Chipman is dealing with equilibria, that in actual practice conditions may be very far from equilibria and that because of this, certain conclusions that we may tend to draw from the work may not be justified.

Specifically, the curves in Fig. 11 and the subsequent reasoning that they involve, lead Dr. Chipman to use the conception of Fe_3C in liquid steel as the base for his further calculations. This is merely a mathematical convenience and it does not necessarily mean that Fe_3C as such is actually present in the melt. Present day knowledge of solutions leads us to believe that carbon in liquid iron may be analogous to a hydrated solution in water, and all we know from the curves in Fig. 11 is that the activities change. Such a change may be due to compound formation or some other type of molecular bonding that would not necessarily correspond to any given stoichiometrical formula.

The FeO carbon reaction is always of interest. Dr. Chipman has shown that the CO_2-CO ratio obtained from his calculations and from the Vacher and Hamilton work are in fair agreement. If CO_2 is one of the end products of the FeO + C reaction, then the equation $FeO + C = Fe + CO$ must always be thought of in conjunction with $CO + \frac{1}{2}O_2 = CO_2$ or some variation thereof. In the work done by Mr. Egan and the writer a much lower equilibrium constant value is obtained and this value is checked by an experiment performed by Vacher and Hamilton in an Arsem furnace rather than an induction furnace. The cause for the difference in value may be found in the fact that in a resistance type furnace molybdenum, for example, would be oxidized by CO_2 so that the atmosphere over the melt would be substantially CO; thus the low equilibrium constant would be correct for the simple reaction $FeO + C = CO + Fe$.

The work on manganese deals entirely with the oxide, although some of the steels with which Dr. Chipman has worked presumably contain sulphur. If sulphur is present there must be an equilibrium between manganese oxide and manganese sulphide. This may well determine residual manganese oxide and even if it does not determine it, it may seriously affect the manganese-manganese oxide equilibrium. The same applies for other sulphide-forming elements such as aluminum, and more especially with zirconium.

If the values given in Fig. 15 are taken at 1600 degrees Cent. the MnO-FeO ratio should be about three. Certain heats have been reported by the writer and his colleagues in TP 498 A.I.M.E. Heat number four described in this paper is a good illustration. The total oxide in this heat corresponds very well with the total oxide in Dr. Chipman's calculations, but instead of having a ratio of MnO to FeO of three, we have a ratio of 1/5. It may well be that this is due to the fact that the heats in question were not in equilibrium but we are inclined to take the view that the discrepancy is too great to be so easily accounted for in this way. Again Dr. Chipman's work shows a certain discrepancy with relation to Herty's work in the silica equilibrium. Silicates are undoubtedly quite soluble in sulphides so that the effective equilibrium value would be modified. This may account for the difference.

In Fig. 18 it is interesting to note that at temperatures of 1600 degrees Cent. and below, the curves are rapidly becoming asymptotic with 0.2 per cent

silicon or more, whereas, experience shows that the degree of killing of the steel does increase with increased silicon addition. This might be taken to be contrary to the curves in Fig. 18. Again, of course, we are probably far from equilibrium.

The curves shown for chromium in Fig. 21 are particularly interesting in the light of those given for silicon. According to these curves there should be practically no chromium loss when a varying amount of chromium is added to a heat of steel containing silicon if equilibrium contents are attained. This is, of course, contrary to practical experience and it is probably the best illustration of the necessity for considering all factors before arriving at conclusions.

Similar observations are true with respect to vanadium. In the summary curve, Fig. 22, we note that 0.01 per cent vanadium will have a killing effect equivalent to that of 0.4 per cent silicon. Experiments show that this is not the case. Again the reason may be that we are far from equilibrium. In this case there is, of course, the possibility of a carbide formation to further complicate the problem. In the case of zirconium the curve is particularly interesting because if the values shown by Dr. Chipman are modified by the high stability of the zirconium sulphides, the total residual oxide in the zirconium treated heat should be still lower and, therefore, zirconium-treated steel should have a lower FeO content than any steel treated with readily available commercial ferro alloys.

In the classical equation 7 of A. L. Feild, rigorously checked by E. R. Jette, slag-metal equilibria play an important role. It is probable that the slag-metal reaction dominates in practice. Even here, however, we may not think in terms of equilibrium because we are probably very far away from it in most cases. In other words, the open-hearth problem is a dynamic rather than a static problem. However, in order to understand dynamic problems it is necessary to have a quantitative comprehension of the statics involved. This work of Dr. Chipman has gone a long way to help us to such a comprehension. With further work of this nature, in the next few years, there is some hope that we will be in a position to attack the problem of the dynamics. Dr. Chipman is to be especially commended for the splendid start along a hard road.

Written Discussion: By G. Phragmén, Metallografiska Institutet, Drottninggatan, Stockholm, Sweden.

Dr. Chipman's calculation of the activity of carbon in liquid steel is of great interest to me, as I have independently tried to approach the same problem. In the discussion of a paper by Vacher and Hamilton[1] on the carbon-oxygen equilibrium he pointed out that the most probable assumption to be made in order to make the thermodynamical calculation of this equilibrium compatible with the experimental results is that the carbon activity is no linear function of the carbon content of the steel. In the discussion of two papers by Yap[2] published at the same meeting I tried to direct the attention to this same possibility. In a textbook on metallurgical thermodynamics[3] a detailed calculation was given.

[1] *Transactions*, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1931, p. 124.

[2] Technical Publication, American Institute of Mining and Metallurgical Engineers, No. 381, No. 382, 1931.

[3] G. Phragmén, *Termodynamik*, Stockholm, 1931, p. 123.

Dr. Chipman has discussed very clearly the possible assumptions on the molecular structure of the solution of carbon in liquid steel and in austenite. He has concluded that the carbon probably forms several kinds of molecules of the type Fe_xC. He has, however, based his calculation on the assumption that the carbon, both in austenite and in liquid iron, is present as Fe_3C.

It should be observed that this assumption is not necessary for the calculation performed by Dr. Chipman. As a general rule, thermodynamical calculations should be brought on as far as possible without any assumption about the molecular structure of the solutions. The necessary assumptions should be introduced at the end.

The assumption of Fe_3C as a solute in austenite is not favored by X-ray work on the crystal structure. The high diffusion velocity of carbon in austenite

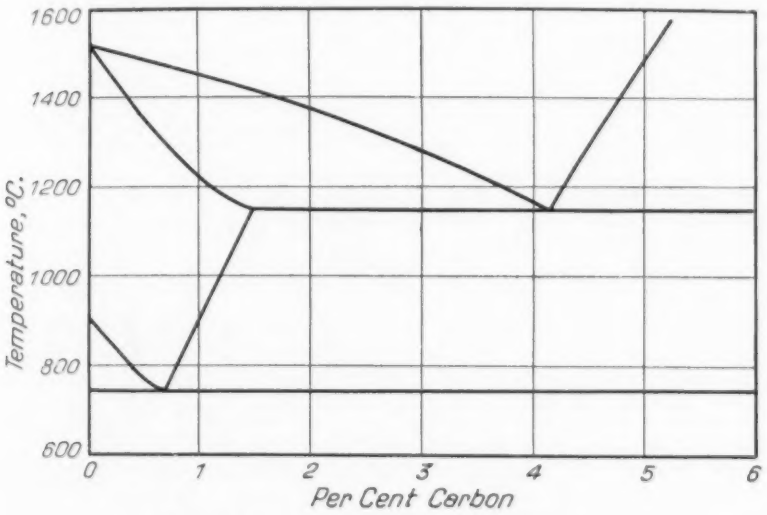

Fig. A—Iron-graphite Equilibrium Diagram.

is also against the assumption of Fe_3C molecules. Dünwald and Wagner have found that the carbon activity is not exactly a linear function of the carbon content of the austenite. It is, however, not astonishing if the austenite deviates from dilute solution.

The real substance of the calculation is this. The carbon activity of austenite as a function of its carbon content has been studied experimentally at temperatures below 1100 degrees Cent. The results have been extrapolated for low carbon contents up to the melting point of iron. The carbon activity is the same in the liquid iron as in the austenite, with which it is in equilibrium. Thus it is possible to calculate the carbon activity along the liquidus.

It is possible to obtain an approximative diagram of the carbon activity in iron-carbon alloys as a function of the carbon content and the temperature in the following way. The iron-graphite equilibrium diagram is reproduced in Fig. A, with some simplifying modifications. The liquidus and solidus lines of austenite are extrapolated, showing the hypothetical metastable equilibrium, which would be observed if the formation of the δ-phase could be suppressed.

Both lines end in the hypothetical melting point of austenite, which must be a little lower than the real melting point of iron.

The solidus line of austenite in this diagram is the curved one obtained from quenching experiments. Some investigators, using the method of cooling curves, have found a straight solidus. It should be observed, however, that it is very difficult to determine the point of complete solidification on a cooling curve.

The liquidus of iron is rather well known and also the liquidus of graphite. The line representing austenite in equilibrium with graphite is only a first approximation; it is to be supposed that this line is at lower carbon contents than the corresponding line of cementite (which is well known) in spite of the opposite view presented in several recent papers.[4]

If the carbon activity is represented by perpendiculars on the temperature composition plane, a three-dimensional diagram is obtained. The tops of these perpendiculars form a system of smooth surfaces. The diagram is illustrated

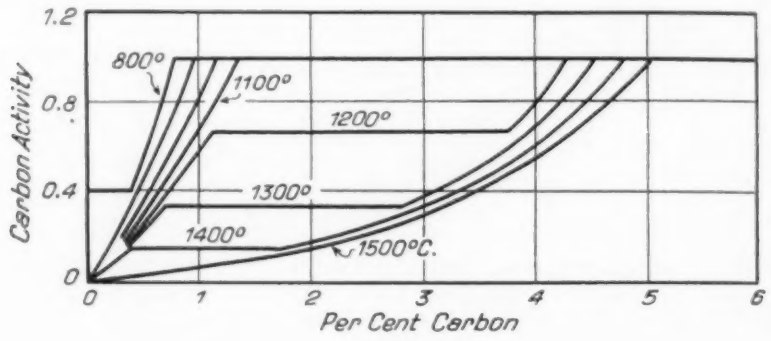

Fig. B

by isothermal sections in Fig. B. Graphite is taken as the standard state of carbon, and thus the carbon activity is equal to unity in all alloys containing graphite as a separate phase. In alloys containing two phases the activity does not depend on the relative quantity of these phases, and in the isothermal sections they are represented by horizontal lines. At 1000 degrees Cent., for instance, the carbon activity increases regularly up to unity at approximately 1.2 per cent carbon and then remains constant. At 1300 degrees Cent. the activity increases in the austenite to about 0.9 per cent carbon, is constant in the austenite + liquid range to 3.1 per cent carbon, increases again in the liquid up to unity at about 4.4 per cent carbon and then remains constant.

The reliability of the activity diagram Fig. B mainly depends on the extrapolation of the carbon activity surface of austenite to high temperatures; it is of course difficult to estimate the reliability of this extrapolation. The correctness of the diagram Fig. A is also very important, especially in regard of the solidus line of austenite.

According to the diagram Fig. B the carbon activity of liquid steel is no linear function of the carbon content. For comparison the carbon activity {C} was calculated as a function of the carbon weight fraction (C) at 1550 degrees Cent. and low carbon contents, according to Dr. Chipman, according to dia-

[4]G. Phragmén, *Jernkontorets Annaler*, 1930, p. 431.

gram B, on the assumption of an ideal solution of C and Fe and on the assumption of an ideal solution of Fe_3C and Fe:

Chipman	{C}	= 3.6 (C)
Fig. B	{C}	= 6 (C)
C and Fe	{C}	= 22 (C)
Fe_3C and Fe	{C}	= 0.5 (C)

The first two results in this table indicate that the carbon in solution is combined with iron to a considerable degree but far from completely. Dr. Chipman has assumed that molten alloys, such as iron-manganese, iron-chromium or silver-aluminum, are very nearly ideal solutions. This assumption surely is the only possible one when nothing is known about the activities. It should be observed, however, that even molten alloys of chemically analogous metals may differ much from the ideal solution. In zinc-cadmium alloys, for instance, if the mol fraction of zinc is 0.1 the zinc activity is 0.3 at 466 degrees Cent.[5] Thus the calculation of the activity of aluminum does not seem very reliable.

DR. C. H. HERTY, JR.:[6] I would like to say a few words about this paper which is, to my mind, one of the best we have ever had on steel making and steel melting.

In the first place, I think that these data on activity and free energy of FeO are extremely important. I know that one of the first things that we were up against when we started our work seven years ago was the absolute lack of data on the temperature effect on the solubility of FeO in iron. We faced the fact that we knew nothing whatsoever about the activity of FeO in liquid iron, and we had to assume that the activity was equal to the percentage by weight of FeO in the iron, and all calculations were based on that.

Dr. Chipman's data indicate very nicely that on all high FeO data that have been accumulated in the past a correction must be made for the activity in making calculations on deoxidation with manganese, etc. Fortunately for almost all commercial steels and irons, the activity is equal to the concentration.

I might mention in connection with Dr. Chipman's work on the equilibrium from which he calculated the activity of FeO, when we first started the solubility work we poured our test into a regular standard open-hearth test mold, and that worked until we got up to about 1600 degrees Cent. Above that we began to reject iron oxide from the steel, even during the pouring of the sample from the induction furnace into the test mold, and at very high temperatures, around 1750 degrees Cent., we formed a very thick scum of iron oxide over the surface of the metal. The metal contained less than it should have so we finally had to pour our test metal into a small wedge test where we took the analysis from the bottom of the wedge where the metal had solidified almost instantly.

The carbon-FeO equilibrium value which Dr. Chipman has determined is significant because we found in low carbon steels, where we calculated 0.01 instead of 0.005, that we could reproduce 0.01 or 0.008 in that neighborhood nicely. Those values were consistent for carbon from 0.05 to 0.15 per cent. At

[5]N. W. Taylor, *Journal*, American Chemical Society, Vol. 45, 1923, p. 2865.

[6]Director of Research, mining and metallurgical advisory boards, Carnegie Institute of Technology, Pittsburgh.

higher carbon contents, 0.60 to 0.80 per cent, the constants were higher as was later indicated by Schuck.

The manganese equilibrium is apparently considerably off. I do not know why because I have not had a chance to talk to Dr. Chipman about it. He finds that with 0.50 per cent manganese in the metal, the metal should contain about 0.45 per cent FeO, and that looks entirely too high to me.

For instance, on low carbon steels at 0.06 per cent carbon, we find that the liquid metal possibly contains 0.29 to 0.30 per cent FeO in the furnace, and then after a manganese addition sufficient to finish 0.40 per cent manganese in the ingot, a spoon test taken from the ladle gives us a value about 0.18 per cent FeO, which is considerably different from the value 0.45 per cent given by Dr. Chipman. On that basis I think the manganese value will have to be revised.

On silicon, I was glad to hear him say that I was high in one case and he was high in the other.

On acid open-hearth Dr. Chipman drew certain conclusions from the dissociation of acid slags based on the manganese equilibrium constant. Three years ago, Mr. Jacobs and I began a series of experiments on acid open-hearth furnaces where we were interested in the FeO content of the metal. We got some very nice data and from those data we calculated that the degree of dissociation of the manganese silicates was very close to ⅛ as high as the degree of dissociation of the iron silicates.

Finally, on the aluminum equilibrium, I will confess now (five years afterwards) that I was very hesitant, and so was Dr. Fitterer, about the aluminum data that we published at that time. We used the hydrogen method for determining oxygen, and we used the best methods at that time for the determination of aluminum. When you get two methods, both of which are shaky, and pile them on top of each other, I am certainly agreed that Chipman is probably far closer than we were at that time.

Dr. Reeve is going to analyze for me a heat of steel which has a residual of 0.026 per cent metallic aluminum. We know the Al_2O_3 content from the electrolytic method. I am hoping that by that particular method we will find out something about the oxygen-aluminum equilibrium and how this value will compare with Dr. Chipman's.

The main point to my mind about this whole paper is not the question of whether or not an equilibrium constant is 3 times as high as somebody's determined constant. What sticks in my mind is that in the past 14 years we occasionally get a paper on steel-making which involves a good deal of thermodynamics, and each succeeding paper is a little better than the one before because we get a little more experimental data.

The first papers that were written on this subject involved the most terrific assumptions that you can imagine, and some of them got the most terrific results.

In any event, with each succeeding paper we get closer and closer to practical facts on this. The important thing from that standpoint is that after enough experimental data are combined with proper calculations such as Chipman has made, we are going to be able to eliminate a large amount of experimental work and calculate some of the things that cost a lot of money and take a lot of time to do.

I think this is a splendid paper and I am glad to see it. I want to congratulate Dr. Chipman on his work.

LEWIS REEVE:[7] I am very sorry that this paper was given to me only this morning. Otherwise, I should have had a much happier time going through it. Undoubtedly it is one of the most complete summaries of equilibrium work applied to steel making that has come out during the last few years. Dr. Chipman is to be congratulated on presenting such a magnificent and clear summary of our present position on this subject. There are one or two points which struck me going through this paper, which perhaps I may comment on, and no doubt on which Dr. Chipman will elaborate.

One point which I have not seen discussed anywhere (and it is not mentioned by Dr. Chipman in this paper) is with reference to a matter which can be understood from the equation given on page 395 with regard to equilibrium between H_2O-H_2-Fe-FeO. I think we can draw some conclusions from this equation which are extremely important from the point of view of the solubility of hydrogen in steel, a matter of considerable importance when it comes to dealing with rimming steels and similar phenomena.

It is a logical conclusion from the equation given on the bottom of page 395, and from the corresponding equations on the following pages, that the solubility of hydrogen in steel containing iron oxide is an inverse function of the iron oxide content of that steel. My reasoning is as follows:

It is apparent that if hydrogen at, say, 1 atmosphere pressure is placed in contact with iron containing iron oxide at some elevated temperature, a certain amount of water will be produced in accordance with the equilibrium equation:

$$(H_2O)/(H_2) = K \times \text{percentage oxygen}$$

Hence, the larger the percentage of oxygen in the iron the larger the extent of oxidation of the H_2 to H_2O. But the amount of H_2 which goes into solution will be proportional to the square root of its pressure: and this pressure has been reduced by its oxidation. Hence the larger the oxygen content of the iron the smaller the amount of hydrogen which will go into solution in it, the exact relationship depending upon the value of y in the equation on page 395.

The point is that there should be some relationship between the hydrogen solubility in steel containing iron oxide and the concentration of the iron oxide in the steel.

This conclusion may explain some of the discrepancies which have been observed in the experimental determinations of the solubility of hydrogen in steel. Referring to the classical work of Sieverts and the controversy with Iwasé in Japan, which, I believe has never been straightened out, it is possible that their differences may have been due to the fact that the electrolytic iron which they used had different amounts of oxygen.

The only other point I want to make is with regard to the relative position of the curves shown on page 431. I have had some experience with regard to the relative stability of the different oxides of the elements mentioned on that page which I have reported in part in a paper presented to the Iron and Steel Section yesterday. I am interested to note a distinct relationship be-

[7]Metallurgical department, A. O. Smith Corporation, Milwaukee.

tween the deoxidation capacity of the elements mentioned on page 431 of Dr. Chipman's paper, and the speed with which the different oxides of these elements were reduced by carbon in my own experiments. This speed is obviously related to the equilibrium pressure of CO produced which, in turn, is a function of the free energy of formation of the oxides. I find that it is much easier to reduce the oxides of chromium and manganese than it is the oxides of aluminum and zirconium.

With regard to the position of silicon, titanium and vanadium, it may interest Dr. Chipman to know that in the case of titanium oxide I found that its speed of reduction did lie roughly between that of the oxides of silicon and aluminum. But with regard to vanadium oxide V_2O_3 I find that it lies almost exactly on the silica curve.

I wish to repeat again that I am very sorry I did not have the opportunity of going through this magnificent paper earlier. It is certainly the most complete one I have read in the last few years.

Author's Closure

Dr. Austin has raised a question as to the applicability of equations such as those on page 411 to conditions other than the standard 1 per cent solution. The answer is that when we specify 1 per cent as the standard reference state we are defining the activity as equal to the percentage; and when the equation is used to calculate the equilibrium constant the result is expressed in per cent. Thus for its main purpose, the calculation of equilibrium constants, this kind of equation is fully applicable to percentages other than one. A more complete answer will be found on pages 291-295 of Reference 6. The difference between Equation 8 and that given in the *Journal* of the American Chemical Society is due to the use of a more accurate expression for the free energy of water vapor. Equation 2 is believed to be more exact than any equation which has previously been published for the free energy of steam at the temperatures in which we are interested.

It is very gratifying to have Mr. Vacher's confirmation of our results on the gas equilibria. Even though the equilibrium constants computed from the two sets of data are not in precise agreement the discrepancy is relatively small and might easily be due solely to a difference of some twenty or thirty degrees in the temperature scales.

I wish to thank Dr. Kinzel for his exhaustive discussion and especially for the emphasis which he has placed upon the fact that conditions are often very far from equilibrium. This is occasionally true even when an apparently steady state has been attained as in Kinzel and Egan's experiments on the carbon-oxygen reaction. It is becoming increasingly apparent that equilibrium was never attained in these experiments and that the low product obtained was due to the sluggishness of the gas-metal reaction at the flat metal surface.

In connection with the manganese equilibrium it should be noted that Figs. 14 and 15 are based upon the average of five independent investigations in which the average deviation is only about 12 per cent. Therefore, if we find in a given case that the equilibrium ratio of MnO to FeO is 3 according to Fig. 15 and 1/5 according to Kinzel's experiments, this means simply

that he disagrees with everyone else who has studied this reaction. This 15 fold discrepancy might be explained either on the grounds that Kinzel's experimental heats were far from equilibrium or that his iodine extraction method leads to entirely erroneous results. Dr. Kinzel rejects the first of these explanations and I am unwilling to accept the second. Actually his experiments have nothing to do with the question except as regards total oxygen content in which he finds some grounds for agreement. It is obvious that, granting the correctness of his analyses, the FeO which he reports includes both that which was dissolved in the liquid steel and that which was present in the suspended particles of FeO-MnO mixture. Now it is only the composition of this non-metallic phase which is predicted by Fig. 15 and not the overall ratio of MnO to total FeO. Therefore, the apparent disagreement is merely an erroneous interpretation which cannot affect the validity either of Fig. 15 or of Dr. Kinzel's experiments.

The curves of Fig. 18 are in no wise contrary to practical experience. Indeed it is well known that 0.2 per cent silicon remaining in the heat as such (not as silicates) is amply sufficient to kill any low-carbon heat under ordinary conditions. No amount of experience could show whether or not a similar heat containing 0.4 per cent silicon is any more thoroughly killed. The time has come when metallurgists must recognize the fact that a heat may be "killed" without being very thoroughly deoxidized. This is a conclusion which probably would never be reached from practical observation but which soon becomes obvious to anyone who will take the trouble to study the actual oxygen contents of steels made under different conditions or deoxidized with different elements.

In the case of chromium there is plenty of opportunity for this alloy to react with the slag even when the bath has been deoxidized with silicon. This is the main source of loss. There are not yet sufficient data for a thermodynamic treatment of the behavior of chromic oxide in slag. This is a case in which a direct experimental attack upon the problem ought to be capable of yielding accurate results.

Dr. Kinzel's remarks in regard to the line for vanadium in Fig. 22 are substantiated by experience. It seems very probable that this line should be considerably higher. The calculations upon which it was based are only approximate and there is little hope of improving their accuracy until someone will prepare a sample of pure vanadium and determine its heat of oxidation.

I confess I find it impossible to follow Dr. Kinzel's argument regarding the effect of zirconium sulphide in modifying the deoxidizing action of zirconium. There is no practical or theoretical evidence to indicate that it has any greater deoxidizing power than aluminum. The position of its line in Fig. 22 is not known with enough precision to determine which of these two elements is the more powerful deoxidizer.

Dr. Herty has correctly pointed out the weakest part of the calculations regarding manganese, namely, the curves of Fig. 16. These curves depend in part upon the rather dubious extrapolation indicated by the broken line of Fig. 6. The discrepancy is by no means as bad as Herty's figures seem to indicate. Fig. 16 shows only the maximum possible percentage of oxygen re-

maining in the presence of manganese. Lower oxygen contents are to be expected as the result of slag-metal reaction or the presence of small amounts of silicon.

It is gratifying to know that Dr. Herty's conclusions regarding the dissociation of manganese silicate are in such good agreement with mine. Further experimental data on the actual degree of dissociation of ferrous silicates would be very helpful in the study of acid slags.

As to the aluminum equilibrium further experimental studies will be interesting but it is exceedingly doubtful if there is any technique available at the present time which will yield results whose accuracy is comparable with that of Fig. 20.

Mr. Reeve has brought up an interesting point in regard to the solubility of hydrogen. His reasoning is clear and correct. His evidence on the reduction of vanadium oxide supports the conclusion that the vanadium line of Fig. 22 is drawn too low.

Finally, I wish to thank Professor Phragmén for his very clear discussion of the activity of carbon. His calculation has the undisputed advantage of being free from all assumptions as to the molecular constitution of the solution. It is interesting to note that this treatment leads to results very similar to those obtained on the assumption that Fe_3C is the principal solute. The small divergence noted in his table would have been even smaller if he had selected the straight-line solidus. The whole question would be greatly clarified by a more rigorous experimental study of the iron-carbon system. In regard to the activities in molten alloys it is always possible that the solution deviates from the ideal law. In general, it is known that at higher temperatures the deviations from ideality become smaller so that the assumptions that have been employed do not appear to introduce any very large uncertainties.

THE LINEAR THERMAL EXPANSION AND α–γ TRANSFORMATION TEMPERATURE (A_3 point) OF PURE IRON

By J. B. Austin and R. H. H. Pierce, Jr.

Abstract

The linear thermal expansion of ten samples of "pure" iron has been determined from room temperature to 950 degrees Cent. by means of a vacuum interferometer. The true expansion coefficient passes through a maximum between 400 and 500 degrees Cent., then through a minimum at the A_2 point at which there is no abrupt change in length. The A_3 temperature of the samples believed to be purest is 928 degrees Cent. Thermodynamic calculations show that the difference between this value and that now accepted is accounted for by the presence in the ordinary samples of small amounts of impurity. The expansion values are in good agreement with existing X-ray data.

ALTHOUGH the thermal expansion of iron has been studied by a number of investigators[1] several points remain doubtful, notably the behavior in passing through the magnetic inversion (A_2 point), the magnitude of the length or volume change accompanying the α–γ transformation, and the true equilibrium temperature of this transformation in pure iron. In an attempt to remove some of these uncertainties we have determined the thermal expansion of a number of samples of pure iron from several different sources, listed in Table I, and have supplemented these observations by measurements of the magnetic susceptibility of several samples in passing through the α–γ transformation. The results show generally that the true expansion coefficient passes through a maximum near 500 degrees Cent. and through a minimum at the A_2 point (768 degrees Cent.); that the equilibrium temperature of the α–γ inversion is close to 928 degrees Cent., about 20 degrees higher than the value now commonly accepted; and that pure iron expands linearly more in chang-

[1]For a summary of previous work of Ralston, Iron Oxide Reduction Equilibria, Bulletin Bureau of Mines 296, 1929. Also Abegg's Handbuch der Anorganischen Chemie, Vierter Band. Dritte Abteilung, Zweiter Teil, A. Lieferung 1, 1931.

A paper presented before the Fifteenth Annual Convention of the society held in Detroit, October 2 to 6, 1933. The authors, J. B. Austin and R. H. H. Pierce, Jr., are associated with the Research Laboratory of the United States Steel Corporation at Kearny, N. J. Manuscript received May 11, 1933.

Table I

Description of Samples

Sample No.	Material	C	Mn	S	P	Si	O†	N	Remarks
1	Burgess double-refined electrolytic iron. Used without treatment.	0.012	.....	.....	0.004	0.013	.....	.....	$H_2 = 0.07$
2*	Westinghouse iron (A185) vacuum-melted electrolytic iron.	.....	.....	.....	.....	0.035	0.003	0.0009	$d_4^{20.8} = 7.864$
3*	Westinghouse iron (A160) hydrogen-melted electrolytic iron.	0.002	trace	0.006	0.012	0.03	.....	.....	.....
4	Open-hearth ingot iron melted in hydrogen.	.....	.....	.....	.....	.....	.....	.....	.....
5**	Armco iron held in moist H_2 at 1500 degrees Cent. for 18 hours.	0.005	0.03	0.003	0.004	0.01	0.002	0.0001	Magnetic permeability about 200,000
6***	Walters iron (V53) vacuum-melted electrolytic iron.	0.012	.....	.....	.....	.....	0.004	.....	.....
7‡	Powdered carbonyl iron melted in moist hydrogen.	.....	.....	.....	.....	.....	.....	.....	$d_4^{23.8} = 7.848$
8‡	Powdered carbonyl iron (raw material same as for No. 7) sintered in moist H_2 at 1500 degrees Cent. for 18 hrs.	.....	.....	.....	.....	.....	.....	.....	$d_4^{28.2} = 7.856$
9	Carbonyl iron plate as received.	.....	.....	.....	.....	.....	0.012	0.0168	$d_4^{24.1} = 7.877$
10‡	Carbonyl iron plate (No. 9) held in moist H_2 at 1500 degrees Cent. for 47 hrs.	.....	.....	.....	.....	.....	.....	.....	$d_4^{24.1} = 7.877$

*Secured through the courtesy of Mr. H. Scott, Westinghouse Elec. & Mfg. Co.

**Secured through the courtesy of Dr. P. P. Cioffi, Bell Telephone Laboratories.

***Secured through the courtesy of Dr. F. M. Walters, Carnegie Institute of Technology.

†By modified Ledebur method of Larsen and Brower, *Trans.*, A.I.M.E., Vol. 100, 196, 1932.

‡Permeability believed to be nearly that of No. 5.

ing from γ to α than it contracts in transforming the reverse direction from α to γ.

The expansion measurements were made with the vacuum interferometer apparatus recently described elsewhere[2] with which it is possible to observe a change in length of $\pm 3 \times 10^{-6}$ centimeters and to determine the transition temperature of the specimen within $\pm$ 2 degrees Cent. The test pieces were quite small, being approximately 5 millimeters in height and 2 millimeters in diameter, a size which insures a uniformity of temperature achieved only with difficulty in other methods. An effort was made to maintain the rate of heating or cooling at 3.0 to 3.5 degrees Cent. per minute but small tem-

[2]Austin, *Physics*, Vol. 3, 1932, p. 240.

porary deviations did occur, the rate occasionally getting as high as 4.0 or as low as 2.0 degrees Cent. per minute. In no case was any difference due to rate observed. Investigators acquainted with the methods of thermal analyses have long recognized that the temperature of such a transformation is far less sensitive to variations in the rate of change of temperature when the specimen is heated than when it is cooled and we believe it worthy of note that with the rates used in this work, which were considerably less than those ordinarily used in thermal analysis, the observed temperatures were reproducible on cooling as well as on heating.

As an independent check on the A_3 point thus observed, the magnetic susceptibility of samples 2, 4 and 8 was determined from 800 to 950 degrees Cent. by a weighing method[3] employing specimens approximately 25 millimeters long and 2 to 5 millimeters in diameter. In order to protect these pieces from oxidation they were plated with a layer of chromium approximately 0.001 inch thick which proved sufficient provided they were not held above 900 degrees Cent. for more than an hour or two. Microscopic examination of a cross-section of the specimens after the measurements were completed showed that the chromium had diffused only to a depth approximately equal to the thickness of the plate, so that the layer containing chromium was only a few thousandths of an inch thick and should therefore not alter appreciably the transition temperature of the specimen as a whole. To minimize any error from this source, however, only the data obtained on heating have been used to fix the A_3 temperature. These observations were limited to the temperature range in which iron is paramagnetic, and yield no definite information about the A_2 or Curie point.

The Expansion Coefficients

Numerical values for the linear expansion coefficient of the several samples are given in Tables II and III, containing respectively the mean coefficient, α_m, between 0 and t degrees Cent. and the true coefficient α_t, at t degrees Cent. These data were derived from a curve representing a graphical average of the observations which included at least 30 points for each sample. The observed transformation temperatures are given in Table IV and Fig. 3, while the

[3] A description of the apparatus will be published shortly.

Table II
Mean Linear Expansion Coefficient

$$\alpha_m \left(= \frac{1}{l_o} \frac{l_t - l_o}{t} \right) \times 10^6$$

Degrees Centigrade

Sample	0 to 100	0 to 200	0 to 300	0 to 400	0 to 500	0 to 600	0 to 700	0 to 800
1	11.7	12.2	13.0	13.8	14.3	14.6	14.7	15.3
2	11.2	12.2	13.1	13.8	14.3	14.6	14.7	14.6
3	11.6	12.4	13.0	13.7	14.4	14.7	14.9	14.9
4	11.2	12.1	13.0	13.7	14.2	14.4	14.6	14.7
5	11.5	12.4	13.0	13.6	14.2	14.5	14.7	14.8
6	11.2	12.2	12.9	13.6	14.0	14.4	14.6	15.0
7	12.0	12.6	13.1	13.7	14.4	14.7	14.8	14.8
8	12.0	12.6	13.1	13.7	14.4	14.7	15.0	15.1
9	11.3	12.6	13.3	13.9	14.5	14.8	14.9	14.9
10	11.7	12.4	13.1	13.8	14.4	14.8	14.9	14.9
Selected Average	11.9	12.3	13.1	13.7	14.4	14.7	14.9	14.9

behavior of each specimen in passing through the inversion is shown in Fig. 2.

From Table III it is evident that the true coefficients for temperatures below about 600 degrees Cent. agree as well as can be expected for such a variety of samples; but at higher temperatures there are considerable differences which indicate that in this region the expansion of a given sample of iron is sensitive to very small changes in composition or previous treatment or both. Consequently a precise general coefficient cannot be given for pure α iron between 600 degrees Cent. and the A_3 transformation point. The average values in Table III for temperatures below 600 degrees Cent. are based on observations on samples 7, 8 and 10 which we believe, for reasons to be given later, are the purest of all. The data for these

Table III
True Linear Expansion Coefficient

$$\alpha_t \left(= \frac{1}{l_o} \frac{dl}{dt} \right) \times 10^6$$

Degrees Centigrade

Sample	100	200	300	400	500	600	700	750	800	850	Gamma Iron
1	12.2	13.7	15.3	16.4	16.3	15.9	....	....	....	....	22.0
2	12.2	13.9	15.2	16.0	16.3	15.5	14.8	14.4	14.3	14.6	22.6
3	12.4	13.7	14.8	15.9	16.7	16.2	15.6	15.3	15.4	15.6	22.2
4	12.1	13.9	15.5	16.0	16.0	15.7	15.3	15.2	15.2	....	22.9
5	12.5	13.8	14.7	16.1	16.4	15.9	15.7	15.5	15.4	15.5	24.6
6	12.3	13.7	15.0	16.0	15.8	16.1	16.8	17.4	18.2	....	22.3
7	12.7	13.8	14.6	16.6	16.8	15.8	15.2	14.8	14.9	15.7	23.3
8	12.7	13.6	14.6	16.7	16.8	16.3	16.1	16.0	16.5	16.8	22.2
9	12.5	14.6	15.1	16.4	16.4	15.9	15.4	14.5	14.8	15.4	22.4
10	12.3	13.8	15.3	16.6	16.8	15.9	15.5	15.0	15.3	16.0	21.6
Selected Average	12.6	13.8	14.6	16.6	16.8	16.0	....	....	....	....	22.5

three specimens, shown graphically in Fig. 1, illustrate the rather unusual variation of a_t with temperature which was observed in most cases. With rising temperature a_t at first increases, passes through a small dip, increases rapidly to a pronounced maximum between 400 and 500 degrees Cent., then falls rapidly to a minimum at the A_2 point; in all a puzzling behavior for which we have as yet no

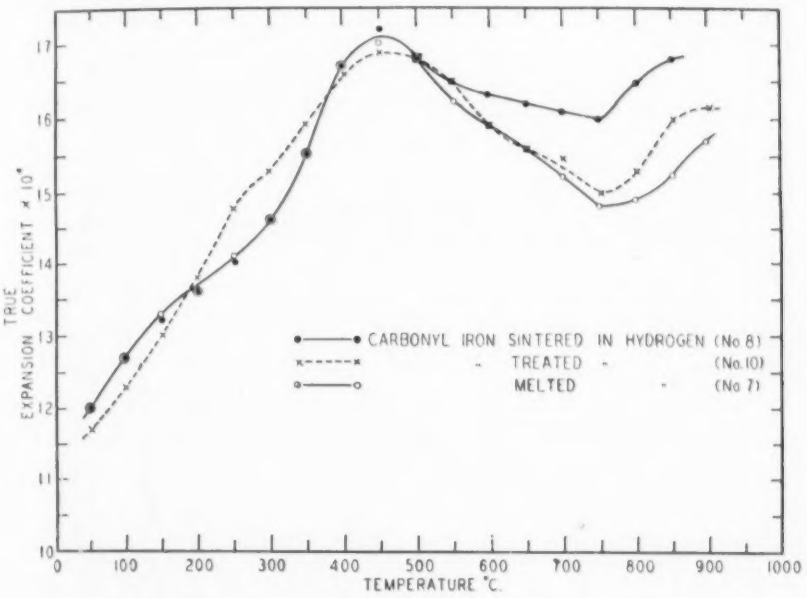

Fig. 1—Temperature Variation of the True Linear Expansion Coefficient.

satisfactory explanation. It is significant, however, that in this same temperature range certain other properties of pure iron appear to show irregularities; for example, the thermoelectric power of iron against platinum shows an abnormality[4]; the magnetostriction passes through a maximum[5]; and hammered iron annealed in this temperature range has a lower density than that annealed at any other temperature.[6] These singularities suggest the existence of some kind of change in iron at these temperatures but the evidence does not warrant any definite conclusion. Further study is to be desired.

Fig. 1 also shows that the coefficients for samples 7 and 8 are in almost perfect agreement while those for sample 10 (hydrogen-

[4]Burgess and Scott, Bulletin U. S. Bureau of Standards, No. 14, 1918, p. 15.

[5]Benedicks, *Journal*, Iron and Steel Institute, Vol. 89, 1914, p. 407.

[6]Ishigaki, Science Reports, Tôhoku Imperial University, Vol. 15, 1925, p. 777.

treated plate carbonyl iron) are higher between 200 and 400 degrees Cent. This suggests that sample 10 may exhibit the slightly abnormal expansion observed in certain hydrogen-treated irons in this temperature range by Rawdon, Hidnert and Tucker[7] especially since they report that one condition favoring the appearance of the ab-

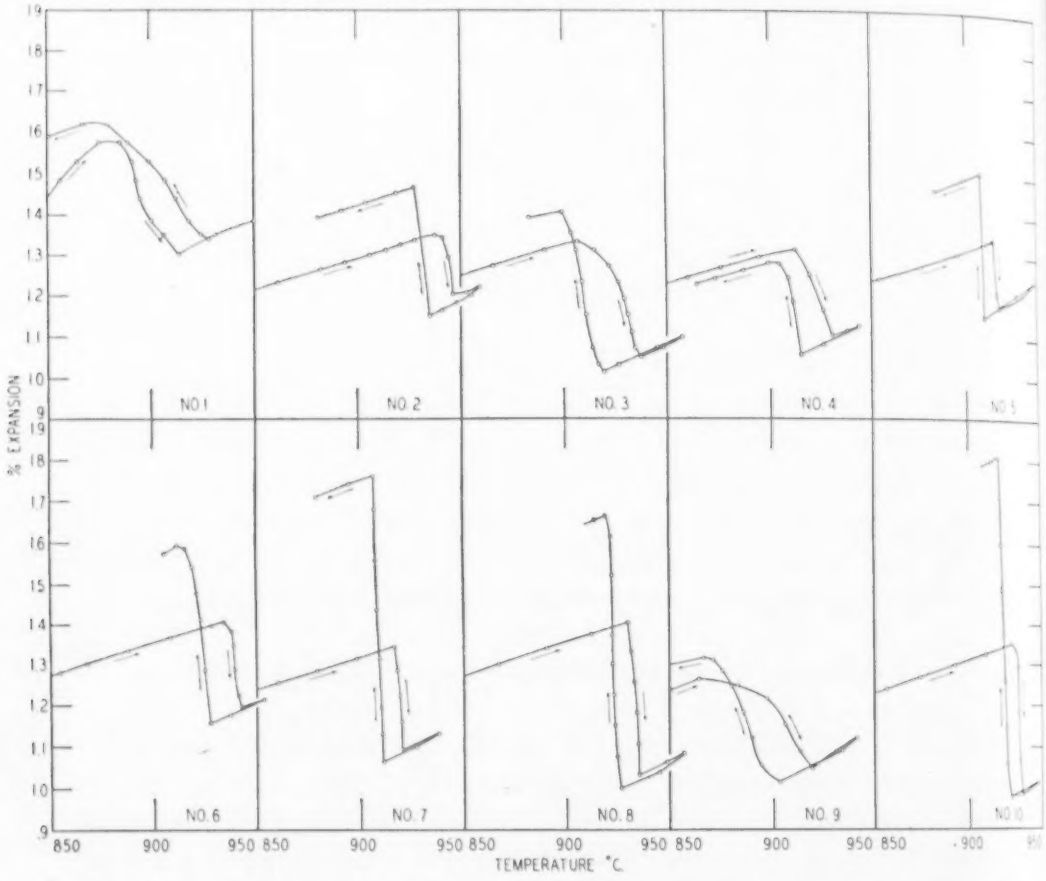

Fig. 2—Length-Temperature Curves for the Several Samples in Passing Through the α-γ Transformation.

normality is the existence of oxide in the untreated metal, and the original iron before treatment had a distinct covering of red oxide.

In view of the difference in purity of the irons examined our average values show reasonable agreement with existing data with the exception of those of Simon and Bergmann[8] who studied the expansion of vacuum-melted electrolytic iron in the range —180 to

[7]Rawdon, Hidnert and Tucker, TRANSACTIONS, American Society for Steel Treating, Vol. 10, 1926, p. 233.

[8]Simon and Bergmann, *Z. physik Chem. Abt. B*, 8, 1930, p. 255.

+50 degrees Cent. and report a true linear coefficient of 15.2 x 10^{-6} at 2 degrees and 16.7 x 10^{-6} at 52 degrees, both of which are nearly 30 per cent higher than our values or any which we have found in the literature. Their work, judging from the very brief published description, appears to have been carefully planned and was carried

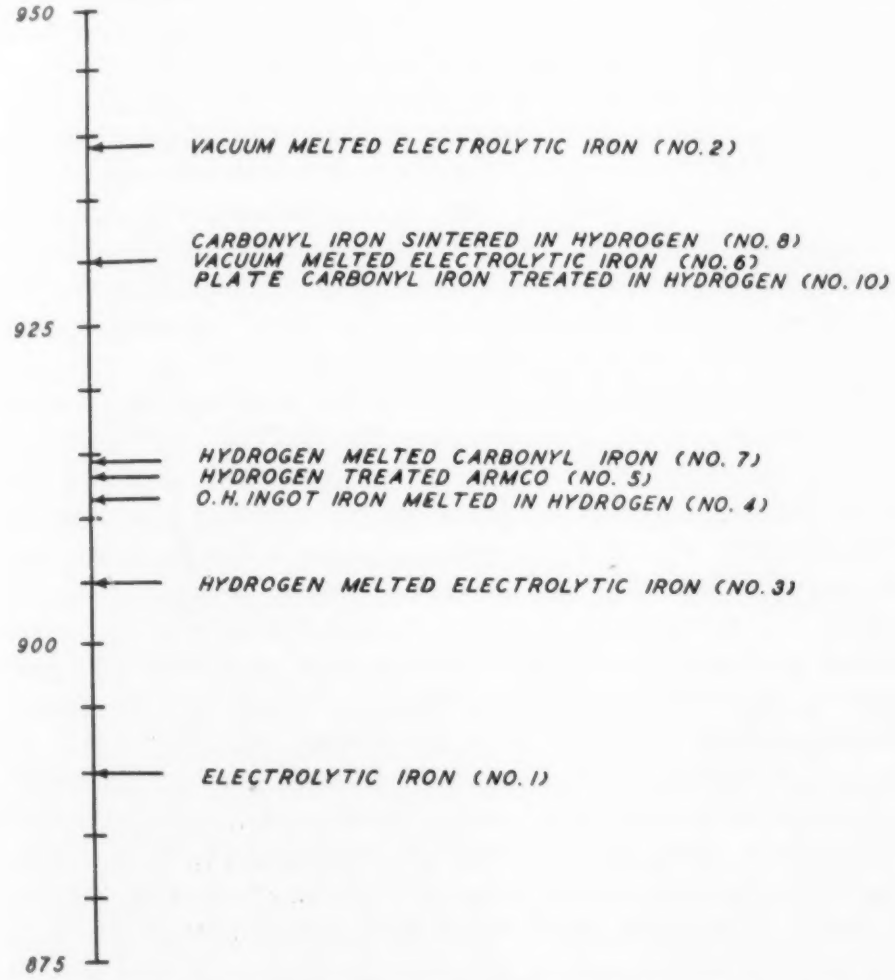
950
925
900
875
VACUUM MELTED ELECTROLYTIC IRON (NO. 2)
CARBONYL IRON SINTERED IN HYDROGEN (NO. 8)
VACUUM MELTED ELECTROLYTIC IRON (NO. 6)
PLATE CARBONYL IRON TREATED IN HYDROGEN (NO. 10)
HYDROGEN MELTED CARBONYL IRON (NO. 7)
HYDROGEN TREATED ARMCO (NO. 5)
O.H. INGOT IRON MELTED IN HYDROGEN (NO. 4)
HYDROGEN MELTED ELECTROLYTIC IRON (NO. 3)
ELECTROLYTIC IRON (NO. 1)

Fig. 3—The α-γ Transformation Temperatures of the Several Samples.

out with iron of satisfactory purity, yet the large discrepancy between their data and all others indicates that their results should not be accepted without reservation. The possible existence of an appreciable error in their measurements leads us to question their report of an anomaly in the expansion of iron, steel and nickel at low temperatures. They state that for all these metals the linear expansion coefficient increases with temperature from –180 to –100 degrees

Cent., is then constant to approximately –30 degrees when it again increases rapidly. No definite explanation is offered for the anomaly or for the high coefficients, and since the anomaly is not confirmed by other investigators who have studied this region[9] we feel that its existence has not been definitely established and that further investigation is needed.

Changes at the A_2 Point

Although above 500 degrees Cent. the expansion of the several samples differs, the general behavior is the same, namely, the coefficient falls to a minimum[10] close to 770 degrees Cent., confirming the observations of Benedicks[11] which have been severely criticized on the ground that they were influenced by a nonuniform distribution of temperature in his apparatus. (It should be noted that our apparatus, which employs very small specimens, is free from most of the objections raised against Benedick's method). A somewhat similar behavior at A_2 has also been observed by Chevenard.[12]

The exact nature of this effect is not certain. Benedicks believed it to be associated with the magnetostrictive effect, that is, with the small but definite increase in length produced in iron by a magnetic field such as is present in the common wire-wound type of furnace,[13] because he had observed that magnetostriction passes through a maximum near 500 degrees Cent. and then falls practically to zero at the magnetic inversion. The correlation between this behavior and the temperature variation of α_t is striking and does suggest that the latter is influenced by magnetic forces, yet Powell[14] has made calculations which indicate that the magnitude of the effect is too great to be explained by magnetostriction alone. The observed changes are, however, of the order of magnitude to be expected from the change in the strength of the binding between atoms which, ac-

[9]Dorsey, *Physical Review*, Vol. 25, 1907, p. 88, and Ebert, *Z. Physik*, Vol. 47, 1928, p. 712.

[10]Note that this is a minimum and not a maximum as stated in Abegg's Handbuch op. cit. p. 125.

[11]Benedicks, op. cit.

[12]Chevenard, *Revue de Metallurgie*, Vol. 14, 1917, p. 625.

[13]The furnace used in the present investigation was operated on alternating current.

[14]Powell, *Proceedings*, Physical Society (London), Vol. 42, 1930, p. 390.

cording to Heisenberg's theory of ferromagnetism, accompanies demagnetization. It is likely that the explanation will eventually be worked out along these lines but the theory is not as yet sufficiently developed to give a satisfactory picture of the mechanical effects associated with the loss of ferromagnetism.

Whatever the cause may turn out to be, it is certain that there is no abrupt change in length at the A_2 point. This conclusion, which is supported by X-ray evidence[15] and is in accord with the zero pressure-coefficient of the A_2 temperature found by Adams and Green,[16] is of interest in connection with the old controversy as to whether or not so-called β-iron (paramagnetic α-iron) should be recognized as a separate phase having a reversible transition to and from α-iron at 768 degrees Cent.

The contention that β-iron is a separate phase appears to be based chiefly on the fact that a considerable amount of energy is absorbed during the magnetic inversion. Since this heat is not absorbed at a single temperature it is necessary on this view to assume a distributed latent heat somewhat similar to that postulated by Sosman[17] for the case of quartz. The concept of a phase, which is primarily a thermodynamic one, has its chief usefulness in connection with thermodynamic calculations and the construction of constitutional diagrams. The properties which distinguish a phase are not precisely defined but the conditions under which two or more phases can coexist are unambiguous. In a one-component system at atmospheric pressure it is possible, according to the Phase Rule, for two phases to coexist in equilibrium at one temperature only. It is obvious from what has been said that insofar as dimensions are concerned there is no singular temperature at which one may properly say that β and α iron are in equilibrium. Hence, there is no phase change, and the loss of ferromagnetism does not imply the appearance of a new phase, at least in the sense in which the term is now commonly accepted. In other words, in a constitutional diagram the curve representing the variation of the A_2 point with composition does not have the same significance as the A_1 and A_3 curves. It merely tells which compositions are ferromagnetic at room temperature and specifies the

[15] See for example, Westgren, *Journal*, Iron and Steel Institute, Vol. 103, 1921, p. 303. Schmidt, Ergebnisse der technischen Röntgenkunde III Wechselwirkung zwischen Röntgenstrahlen und Materie 1933, p. 194.

[16] Adams and Green, *Philosophical Magazine*, Vol. 12, 1931, p. 361.

[17] Sosman, "The Properties of Silica," Chemical Catalog Co., New York, 1927, p. 310.

maximum temperature to which this property can be retained. Consequently, an intersection of the A_2 curve with the A_3 curve indicates only the limiting composition exhibiting ferromagnetism and does not represent a singular point on the latter curve. The diagrams frequently seen in which the A_3 curve changes direction suddenly at its junction with the A_2 curve are, therefore, not justified.

Temperature of the α–γ Transformation

It is immediately evident from Table IV and Fig. 3 that there are considerable and rather disconcerting differences in the observed transformation temperatures of the several samples; but it is noteworthy that most of them are well above 906 degrees Cent., the value which appears to be most widely accepted at present. In view of this variation the selection of a precise value for the A_3 point in "pure" iron becomes a matter of recognizing the "purest" sample in a collection of irons most of which are of extraordinary purity judged by commercial standards. Any decision based on what little is known of the precise composition of the samples is dangerous as well as difficult, since the analyses are obviously incomplete and even the scant information available is no more reliable than the admittedly inadequate analytical methods used in the determination, which, although they have a certain usefulness in indicating the order of

Table IV

α-γ Transformation Temperatures

Sample No.	Material	A_3 Temperature in °C. From Expansion Ac_3	Ar_3	From Magnetic Susceptibility Ac_3
1	Burgess electrolytic iron	890°	912°	...
2	Westinghouse vacuum-melted electrolytic iron (A185)	938	935	938
		943	937	
		949	935	
3	Westinghouse hydrogen-melted electrolytic iron (A160)	904	920	...
		906	911	
4	Open-hearth ingot iron melted in hydrogen	912	915	917
		917	915	
5	Armco iron held in moist H_2 at 1500°	915	911	...
6	Walters vacuum melted electrolytic iron (V53)	930	927	...
		933	925	
7	Carbonyl iron melted in H_2	915	913	...
		916	911	
8	Carbonyl iron sintered in H_2	930	927	928
		930	929	
9	Carbonyl iron plate	864	903	...
10	Carbonyl iron plate treated in H_2	928	927	...

Selected value based on samples 8 and 10, 928° ± 2°C.

magnitude of the amount of a given impurity, are not to be trusted too much in comparing metals in which the given impurity is present in minute quantities. One criterion which might have been a valuable aid in determining the relative purity of the samples is the temperature coefficient of electrical resistance, but unfortunately most of the samples were in a form which made satisfactory resistance measurements impossible and our supply of them was in nearly every case so limited that we could not readily reduce them to a suitable form. We are forced, therefore, to turn to the internal evidence of the curves of Fig. 2. General considerations of the behavior of substances undergoing a polymorphous transition lead to the conclusion that the purest sample is that which on heating shows the sharpest break in the length-temperature curve. A plausible secondary criterion is that the divergence between the sharp break obtained on heating and on cooling, in each case at a definite rate, will be smaller the purer the sample. Judged by these criteria the carbonyl iron sintered in hydrogen (No. 8) and the plate carbonyl iron treated in hydrogen (No. 10) are the best, a result which is not surprising since the carbonyl iron is undoubtedly the purest raw material used in preparing any of the samples, and treatment of a solid sample in hydrogen would not be expected to introduce an appreciable amount of impurity. Sample No. 7 (powdered carbonyl iron melted in hydrogen) had an equally sharp break, but the divergence between the transformation temperatures on heating and cooling was somewhat greater. Since our results for No. 8 and 10 are in excellent agreement, we have selected their transformation temperature, 928 $\pm$ 2 degrees Cent. as closest to the true A_3 point for iron. While we are convinced that 928 degrees Cent. is a better value than any now widely favored we should like to emphasize that it should not be regarded as final, since the criteria by which we judged which sample was purest may be insufficient. It has been reported[18] that Esser has observed an A_3 temperature of 935 degrees Cent. on iron but we have been unable to locate a complete account of his work. Very recently, Hensel and Larsen[19] extrapolating from observations on specially treated samples have estimated that the A_3 point in pure iron is 10 to 20 degrees higher than the datum now accepted, but their results do not permit the assignment of an exact general value.

[18]Hensel, Discussion of a paper by Yensen and Ziegler, *Transactions*, Iron and Steel Division, American Institute of Mining and Metallurgical Engineers, Vol. 95, 1931, p. 923.

[19]Hensel and Larsen, *Metals and Alloys*, Vol. 4, 1933, p. 37.

As a check on these transformation temperatures the A_3 point in samples 2, 4 and 8 was determined magnetically. The results, plotted as reciprocal susceptibility vs. temperature, are shown in

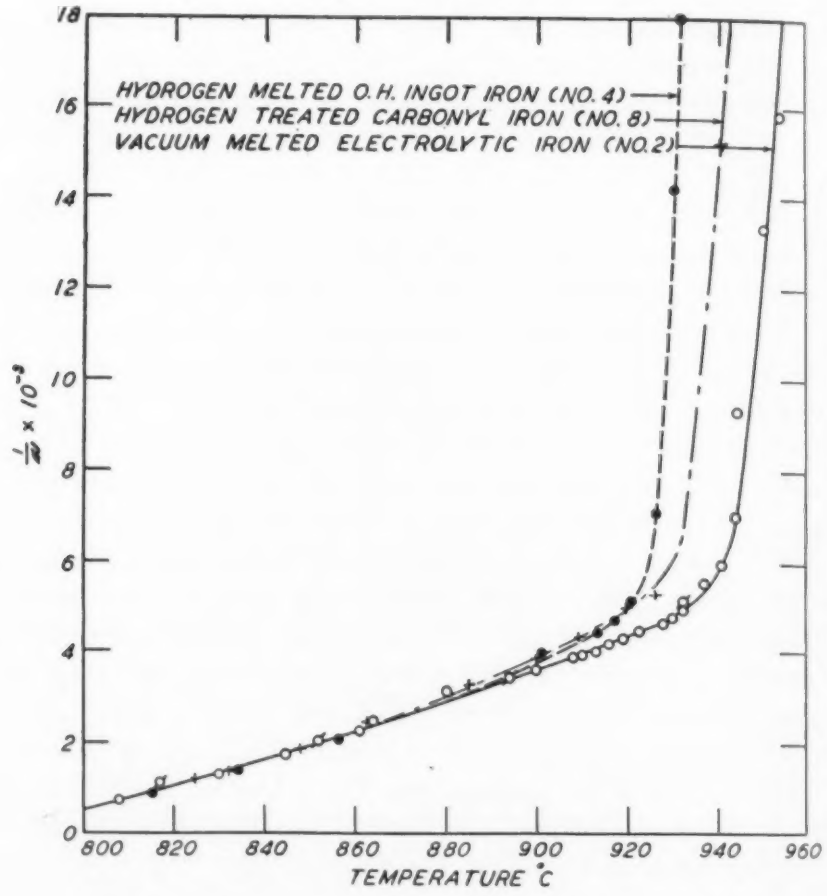

Fig. 4—Temperature Variation of the Magnetic Susceptibility of Samples 2, 4, and 8, Plotted as Reciprocal Susceptibility Versus Temperature.

Fig. 4. The critical temperatures read from these curves are included in Table IV and show good agreement with those determined with the interferometer.

Effect of Impurities on the A_3 Temperature

At first glance it appears possible that the high inversion temperatures may be due to dissolved hydrogen, but a simple calculation shows that this is extremely improbable. Since we are dealing with relatively small quantities of impurity we can apply the following

Table V
Length Change at the A_3 Point

Author	Year	$\frac{\Delta l}{l_o} \times 10^3$	
Svedelius	1898	0.56—0.70	
Le Chatelier	1899	2.6	
Driesen	1914	1.9	heating
Benedicks	1914	0.82	heating } Calculated from
		Ca 2.7	cooling } his figure
Chevenard	1917	2.2	
Souder and Hidnert	1922	1.31	heating
		0.16	cooling
Sato	1925	2.82	heating and cooling
Schmidt	1933	2.6	X-rays
This research	1933	2.6	heating and cooling

Svedelius, *Phil. Mag.* (5) 46, 173 (1898)
LeChatelier, *Compt. rend.* 129, 331 (1899)
Driesen, *Ferrum*, 13, 27 (1914)
Benedicks, op. cit.
Chevenard, op. cit.
Souder and Hidnert, Bull. Bur. Standards, 17, 611 (1922)
Sato, Sci. Repts. Tôhoku Imp. Univ. 14, 513 (1925)
Schmidt, op. cit.

thermodynamic equation which, though long used to estimate the lowering of the freezing point of dilute aqueous solutions, does not appear to have been widely utilized in considering the analogous case of the change in transformation temperature of dilute solid solutions, a case to which it is equally applicable.

$$\frac{dT}{dN_2} = \frac{RT^2}{\Delta H}(K-1) \qquad (1)^{20}$$

where dT is the change in transition temperature T (on the absolute scale) with N_2, the mol fraction of solute in the gamma phase, R is the gas constant per mol of solvent, ΔH is the molar heat of transition and K is the distribution coefficient of the solute between the two phases, that is, the ratio of the equilibrium concentration of solute in the α phase to that in the γ phase at the same temperature; all these quantities being expressed in appropriate units (see Table VI). Equation (1) is reduced to a more convenient form by replacing $RT^2/\Delta H$ by its numerical value for iron thus

$$dT/dN_2 = \frac{1.989 \times (1201)^2}{216}(K-1) = 1.33 \times 10^4 (K-1) \qquad (2)$$

or

$$dT = 1.33 \times 10^4 \, dN_2 \, (K-1) \qquad (3)$$

[20] See, for instance, Lewis and Randall, Thermodynamics, McGraw Hill, N. Y., 1923, p. 238.

Table VI
Lowering of the A_3 Temperature Produced by 0.01 Per Cent by Weight of Impurity as Calculated from Equation 1

$\Delta H = 216$ cals/g-atom $R = 1.989$ cals/g atom/°C. $T = 928$°C. $= 1201$°K

Impurity	$N_2 \times 10^{-8}$	K	dT°C.	Source of Data
H_2 (sat'd)*	0.014	½	−0.09°	Martin, Luckemyer-Hasse and H. Schenck
N_2**	0.40	$\frac{1}{10}$	− 5	Martin, Sieverts and Jurisch
O_2**	0.35	about 1†	nearly 0	Mathewson, Spire & Milligan, Reschka, Scheil, Schulz
C	0.47	1/20	− 6	Estimated from diagram of Körber and Oelsen***
Mn	0.10	..	−1.3	Taken approximately same as carbon
P	0.18	1	.....	
Si	0.20	1	.....	
S	0.17	no data	.....	

*Contains 0.0004 per cent by weight.
**Assumed to be monoatomic in solution.
***See Austin, *Metals and Alloys*, Vol. 4, 1933, p. 49.
†The data for oxygen are very unsatisfactory and this estimate is only tentative.
Martin, *Arch. Eisenhüttenwesen*, 3 (1929/30) 407.
Luckemyer-Hasse and H. Schenck, *Archiv. Eisenhüttenwesen*, 6, 209 (1932-33).
Sieverts and Jurisch, *Stahl and Eisen*, 34 (1914) 252.
Mathewson, Spire and Milligan, TRANSACTIONS, American Society for Steel Treating, 19, 66 (1931).
Reschka, Scheil, Schulz, *Arch. Eisenhüttenwesen* 6, 105 (1932).

The data on the solubility of hydrogen in iron, which appear to be accurate enough for our purpose, have been reviewed by Schenck.[21] On this basis it appears that if both phases are saturated with hydrogen under 1 atmosphere pressure the transition temperature is lowered by only 0.1 degree Cent. (cf. Table VI). Saturation with hydrogen cannot, therefore, explain the observed increase.

Equation (3) can also be used to estimate the effect of other impurities upon the transformation temperature provided the distribution coefficient can be estimated either from direct observations or from the lines of the equilibrium diagram. Taking such data as we have found in the literature, we have calculated the change in T produced by 0.01 per cent by weight of each of several impurities commonly present in iron, with results shown in Table VI.

It is rather surprising to find that the calculated effects are much larger than experience with aqueous solutions at room temperature would lead us to expect; although it has long been known that the melting point of copper is lowered 20 degrees Cent. by the presence of a relatively small amount of oxygen. An inspection of equation (1), however, discloses several factors tending to increase the effect

[21]Schenck, *Physikalische Chemie der Eisenhüttenprozesse*, J. Springer, Berlin, 1932.

of impurities in iron at high temperatures. First the change in transformation temperature dT is proportional to T^2, and should increase rapidly at high temperatures; again it is inversely proportional to ΔH and the heat of the A_3 transformation is very small compared to the heat of fusion of ice. The distribution coefficient is also an important factor so that while the actual concentration of impurity may be small in either phase, the ratio of the concentrations in the two phases may be quite large, as in the case of nitrogen, and thus exert a considerable influence on dT. It should be noted that the sign of dT is determined by the factor (K—1) since the other factors in equation 1 are always positive. If K is greater than 1, that is, if the concentration of solute in the alpha phase is greater than that in the gamma phase, dT is positive, or the transition temperature is raised; on the other hand, if K is less than 1, dT is negative and the transition temperature is lowered. For the case of identical solubility in each phase $K = 1$ and $dT = 0$. When $K = 0$, that is, when the solute is insoluble in the α phase, equation (1) becomes identical in form with the well-known van't Hoff equation for the lowering of freezing point of a dilute solution. It is also worth noting that for the dilute solutions considered dT depends not upon the nature of the solute but only on its molal concentration, hence all solutes for which $(K - 1)$ has about the same value, produce the same lowering of T per mol of solute in the gamma phase (or for equal mol fractions), and the effect of any combination of such impurities is approximately additive in the algebraic sense. Thus, if the impurity present is largely of a kind that lowers T, it is easily possible that the net effect will be a lowering of the transition temperature large enough to account for the difference between the temperature ordinarily observed and accepted and that which we have found in the specimens of carefully purified iron. On the other hand, if the impurities are evenly divided between those that raise T and those that lower it the net result may be no change, or $dT = 0$. In fact, we are inclined to believe that sample 6 which transforms close to 930 degrees Cent. is an example of this case, although the rather unsatisfactory analytical data available point to a slight lowering of T. To sum up, Table VI shows clearly that the presence of very small quantities of foreign matter which are not unlikely to be present in iron may influence the transition temperature more than has been realized, and the effect of nitrogen is particularly notable in this respect.

The temperature 938 degrees Cent. observed on Westinghouse

iron (A185) suggests that the predominant impurities are elements for which $K > 1$ and dT is consequently positive. Of these elements silicon is known to be present to the extent of 0.035 per cent and it seems very likely that it provides the key to the behavior of this sample. If this is true it will necessitate some revision of current ideas of the iron-silicon equilibrium diagram according to which at least 10 times this amount of silicon is necessary to raise the A_3 point by 10°. It must not be forgotten, however, that in this case we are dealing with iron which is relatively free from impurities other than silicon; indeed, it can be regarded as "dilute" iron-silicon alloy with far more justification than can many of the alloys so described in the literature. In fact our results for this sample indicate that the diagrams commonly given should be regarded not as for the binary system Fe-Si but as sections through the system Fe-Si-C, the broadening of the γ loop being entirely analogous to the effect of carbon in the Fe-Cr system.[22] These deductions are in harmony with the experience of others who have found that the α-γ transformation temperature of these alloys rises as the carbon content falls.

In passing it should be noted that the α-γ transformation was observed in every case and with increasing purity tended to become more, rather than less, marked.

We should also like to point out that those impurities which have the greatest effect on the magnetic properties at room temperature are not necessarily those that have the greatest influence on the α-γ transition temperature: thus of the four samples which appear to have a very high permeability, two transformed at 915 and two at 928 degrees Cent. That this should be true is not surprising, however, since the magnetic measurements show (Fig. 4) that above the A_2 point the susceptibility (hence the permeability) of the originally highly magnetic metal is the same as that of the other specimens; in other words, the remarkably high permeability is lost in passing through the Curie point.

Another point worth mentioning is that all the samples melted in hydrogen have a lower transformation temperature than those melted in vacuo or sintered in hydrogen (see Fig. 3—the best comparison being between samples 7 and 8, the powdered carbonyl iron, respectively melted and sintered in hydrogen). This fact we regard as an indication that molten iron in the presence of hydrogen

[22]See Bain, TRANSACTIONS, American Society for Steel Treating, Vol. 9, 1926, p. 9.

is a strong reducing agent and tends to become contaminated through attack on the crucible. On this basis the presence of silicon in the vacuum-melted Westinghouse iron A185 may mean that molten iron alone is capable of reducing SiO_2 while in the presence of hydrogen other oxides also are reduced. These inferences, admittedly based on indirect evidence, are supported, however, by other observations. For instance, Mr. Larsen of this laboratory has found that at 1100 degrees Cent. hydrogen reduces silica in the presence of iron vapor. It appears, therefore, that in purifying iron it is preferable not to melt the sample; but if this cannot be avoided, great care should be exercised to select that refractory which is hardest to reduce and which contains the smallest amount of reducible impurities. A convenient method of obviating some of these difficulties is to hang the specimen to be purified in a vessel through which hydrogen flows and then heat it by means of an induction furnace. If crucibles must be used, BeO and ThO_2 appear to be promising materials.

Change in Length at the A_3 Point

It is immediately evident from Fig. 2 that there are very large differences in the change in length of the several samples in passing through the inversion. There is also in the purest samples a striking tendency to expand more on cooling than they previously contracted on heating, producing a permanent slight increase in length. In view of these facts we conclude somewhat paradoxically that pure iron is not a suitable material for measuring the change in macroscopic linear dimensions of iron at the A_3 inversion, since the change appears to be neither reversible nor predictable. It would be very interesting to learn if measurements of the change in lattice parameter or the volume expansion at this point would be more reproducible. The one sample giving satisfactory results was the open-hearth ingot iron melted in hydrogen (No. 4) for which the maximum and minimum length changes in passing through the inversion were 0.28 and 0.24 per cent respectively. The average of these values, 0.26 per cent, corresponding to an average volume change of 0.78 per cent, is in fair agreement with data of previous investigators (Table V).

This peculiar permanent increase in length of the pure specimens has been observed by many investigators.[23] Seigle, using circular rods, reports that as the length increases, as the result of re-

[23]For example, Benedicks, op. cit.; Stäblein, *Stahl und Eisen*, Vol. 46, 1926, p. 101; Ruf, *Z. Elektrochem.*, Vol. 34, 1928, p. 831; and Seigle, *Revue de Metallurgie*, Vol. 29, 1932. p. 169 and 252.

peated passages through the inversion, the cross section tends to become oval while the volume remains sensibly constant. He ascribes this behavior to a preferred orientation of the grains of the specimen, a view also held by Stäblein. This proposal is not, however, very satisfactory since it is difficult on this basis to see why the anomaly is not more generally observed in impure irons, or iron alloys. Benedicks, whose specimens were in tension, suggested that the irreversibility is caused by a stretching of the metal under the load since it is well known that iron is very soft near the inversion. This interpretation must also be rejected since in Seigle's measurements as well as our own the specimens were under slight compression. We are left, therefore, without an adequate explanation of this behavior. Further study of the subject, preferably by means of volumetric measurements, is needed. The sample of Burgess electrolytic iron (No. 1) showed an abnormal growth or increase in length below the A_3 point which may be associated with a puffing due to evolution of occluded hydrogen or with a recrystallization, the evidence not warranting a definite conclusion.

Other Inversion Points

The only critical points observed below 1000 degrees Cent. were the well-established magnetic and α–γ inversions, unless one chooses to interpret the maximum coefficient near 500 degrees Cent. as indication of one, a view which is hardly justified by present evidence. The sudden break in the dilatation at 370 degrees Cent. reported by Sirovich[24] was not confirmed, neither was the critical point at 830 degrees Cent. suggested by Benedicks, although it is true that in some of the samples the coefficient becomes practically constant at about this temperature after passing through the minimum at 770 degrees Cent. In all the samples examined the A_3 point was single, no evidence being found to support the double-inversion suggested by Harrington and Wood.[25] In fact the behavior of the pure samples indicates so clearly the existence of but one that we feel justified in questioning their interpretation of their results.

Comparison of Expansion Measurements With X-ray Data

Assuming the density of pure iron at 25 degrees Cent. to be 7.865, which is the average density of our best samples, the lattice

[24]Sirovich, *Gazz, Chim. Ital.*, Vol. 53, 1932, p. 674.

[25]Harrington and Wood, TRANSACTIONS, American Society for Steel Treating, Vol. 20, 1932, p. 529.

parameter is calculated as 2.858 Å. U., in good agreement with most of the X-ray measurements at room temperature.[26] Using these values and the average increase in length between room temperature and 928 degrees Cent. we have calculated the density of alpha iron at the inversion point to be 7.520 and the corresponding lattice parameter to be 2.900 Å. U., in agreement with the X-ray measurements of Westgren[27] (2.90 Å.U.) and of Bach[28] (2.8995 and 2.9041) but somewhat higher than the result reported by Schmidt[29] (2.8893 Å.U.). The density of gamma iron at the same temperature computed from the fractional volume contraction of sample 4 (0.78 per cent) is 7.58 and the lattice parameter is 3.64 Å.U., one per cent higher than Westgren's first value of 3.60 Å.U. but in agreement with his later figure of 3.63 and with the data of Bach (3.653) and of Schmidt (3.638). Making the plausible assumption of a constant expansion coefficient of 22.5×10^{-6} for gamma iron between 928 and 1400 degrees Cent. we obtain a density of 7.330 and a lattice parameter of 3.68 Å.U. at the A_4 point which compares favorably with other values (Westgren 3.68, Bach 3.688, Schmidt 3.680). The mean expansion coefficients calculated by Schmidt from his X-ray data are lower than ours and those of most other investigators. Whether this discrepancy is real or is due to the difference in method is not evident. In this connection we should like to call attention to the marked increase in expansion coefficient above 700 degrees Cent. reported by Schmidt for his material which was electrolytic iron. His results are quite similar to those which we obtained with sample 1 (Burgess electrolytic iron) and which we believe are associated with recrystallization or evolution of occluded gas. Since this anomalous effect was not observed with our best samples and is not reported by other investigators we suspect that it is characteristic of electrolytic samples only and is not a true property of iron.

Bach, examining the diffraction patterns of two kinds of iron wire at temperatures between 730 and 1400 degrees Cent., found what he believed to be a contraction of the lattice in passing through the A_2 point; for the first one the lattice parameter decreased from 2.9004 at 730 degrees Cent. to 2.8995 at 785 degrees Cent. while for the

[26] See Ewald and Hermann, Strukturbericht, *Zeit. Kristallographie* 1931, Akademische Verlagsgesellschaft, Leipzig, p. 66.

[27] Westgren, op. cit.

[28] Bach, *Helv. Phys. Acta.*, Vol. 2, 1929, p. 95.

[29] Schmidt, op. cit.

other the decrease was from 2.9071 at 830 degrees Cent. to 2.9043 at 860 degrees Cent. The large discrepancy in the temperatures reported for the A_2 point leads one to suspect serious errors in his temperature measuements which were made with an optical pyrometer. Moreover, the decrement in length of the unit cube is very small, being at the largest only 0.1 per cent. Considering the difficulties involved in securing reliable X-ray data at such temperatures the differences reported must have been very close to the limit of experimental error, so that we do not feel warranted in drawing conclusions from his results as they stand.

Conclusions and Summary

1. The linear thermal expansion of 10 samples of "pure" iron has been determined from room temperature to 950 degrees Cent. by means of an interferometric method in vacuo. The true expansion coefficient passes through a maximum between 400 and 500 degrees Cent. then through a minimum at the A_2 point (768 degrees Cent.). Below about 600 degrees Cent. the expansion coefficients of the several samples are in reasonable agreement but above this temperature there are significant differences indicating that in this range the expansion of pure iron is sensitive to traces of impurity or to the previous treatment of the specimen. There is no abrupt change in length at the A_2 point.

2. The α-γ transformation temperature of the samples believed to be purest is 928 degrees Cent. which is about 20 degrees Cent. higher than the value now generally accepted for pure iron. Thermodynamic calculation shows that the difference between these values is accounted for by the presence of other elements, in amounts aggregating not more than 0.03 or 0.04 per cent by weight, which are practically certain to be present to this extent unless specifically removed by special treatment.

3. It is shown that the change in length observed during cooling through the A_3 inversion is, for the purest samples, always greater than the contraction on heating, leading to a permanent increase in length. For less pure samples the average change in length in passing through the inversion is 0.26 per cent of the length at room temperature.

4. The well-established A_2 and A_3 points were the only critical points observed.

5. The expansion data are in good agreement with existing X-ray evidence.

6. The results indicate that those impurities which appear to have the greatest influence on the magnetic properties at room temperature may or may not shift the α-γ transformation temperature appreciably.

7. There are indications that pure iron melted under hydrogen becomes contaminated through reduction of the crucible material. Melting in vacuo or sintering in hydrogen gives a better product.

It is a pleasure to acknowledge our indebtedness to Mr. Howard Scott and to Dr. P. P. Cioffi for help in securing samples and for suggestions on the interpretation of the results. We also wish to thank Dr. F. M. Walters for the sample of iron made by him.

DISCUSSION

Written Discussion: By N. A. Ziegler, Westinghouse Electric and Manufacturing Co., Research Laboratories, East Pittsburgh.

Messrs. Austin and Pierce should be complimented for their very instructive paper. It is very interesting to know that the A_3 point in iron actually does go up with increasing purity, which confirms previous reports of Hensel and of Esser. Whether or not it will go still higher up with increasing refinement remains to be seen. The sharpness of A_3 point in the purest samples speaks in favor of the allotropic transformation being an "inborn" property of pure iron.

It is surprising to know that Westinghouse irons, vacuum- as well as hydrogen-melted, show such high contents of impurities. The average analysis of eight independent ingots of hydrogen-melted iron (corresponding to No. 3 in the paper) is as follows:

S	P	Mn	Si	Cr	Ni	Mo	Cu	C**	O_2*	N_2*	H_2*
0.008	0.003	0.002	0.003	←———	None	———	→	.0010	.0015	.0006	.0002

*Vacuum fusion method. **Yensen method.

Only one ingot, prepared in a soft crucible, had 0.010 per cent silicon, but it has not been used.

Vacuum-melted iron (corresponding to No. 2 in the paper) has practically the same analysis, except that its oxygen may be a little higher (up to 0.003 per cent), providing that the melt has not been deoxidized by adding small amounts of carbon.

It is not at all clear, why values for silicon and phosphorus should be as high as given in the paper (Table I).

The observation of irregularities of almost all properties at about 450 degrees Cent. is extremely interesting. Could it not be possible, that this is the beginning of the magnetic transformation, the end of which is A_2 point? This may be confirmed by the observation of the authors that there is no abrupt change of properties at A_2 point.

The remark that the chemical analysis in this case is not very reliable due to very minute amounts of impurities present, is very logical, but the sharpness of the break in the length-temperature curve is hardly a good criterion of the purity either, because as it was pointed out before by Masing it also is a function of the grain size and orientation.

According to our observations, silicon even up to 0.035 per cent will not have any effect on the position of A_3 point in iron.

H. W. McQUAID:[1] This paper is, to me, highly theoretical, and not being as theoretical as I should, it looks like it is a starting point for a lot more work. Of course it is impossible in practice to get any irons that approach these in purity, or to use these.

I wish the next step would be to take this material and determine what the effect of oxygen is and what effect different percentages of FeO in solid solution would have on these expansion rates and on the critical changes and critical point changes, etc.

R. H. HARRINGTON:[2] May I read two sentences in the authors' paper?

"In all the samples examined the A_3 point was single, no evidence being found to support the double-inversion suggested by Harrington and Wood. In fact the behavior of the pure samples indicates so clearly the existence of but one that we feel justified in questioning their interpretation of their results. . . ." The theoretical interpretation offered in the publication of ours, to which the authors refer, quite plainly shows that only one of those points would be discoverable by this method of expansion measurement, and also the authors are dealing with iron which is quite likely more nearly pure. A good many impurities may cause this doubling, and the mere fact that only one point can be found on expansion measurements does not at all affect the theory or real appearance of a doubled A_3 point.

I would also like to point out that recent work has been done on this by Esser and Cornelius. They have shown that treatment in hydrogen will cause doubling, which may be discoverable by thermal analysis. A heat treatment in vacuum will remove the hydrogen, and this may be checked by thermal analysis. Since the work that we had done was also performed in vacuum, we feel that hydrogen was not the impurity that caused the doubling in our work. However, some other minor impurities may have been the cause.

We should like to point out that we do not feel that the behavior of these "pure" samples tested in this way by expansion measurements could so clearly indicate the existence of only one point, except as interpreted that that point is the thermal expansion point. With a clear understanding of our (Wood and Harrington) interpretation of a doubled A_3 point, it does not seem that the authors of this most interesting paper are justified in making the two statements quoted from page 464 of their paper.

F. M. WALTERS:[3] Those of us who have not worked with interferometers cannot appreciate the experimental difficulties which Austin and Pierce have overcome in the work described in this paper.

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[1]Republic Steel Corp., Detroit.

[2]General Electric Co., Research Laboratories, Schenectady, N. Y.

[3]Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh.

The authors have observed that with the purest irons, the expansion on cooling through A_3 is greater than the contraction on heating. This observation is very interesting because when sample No. 6 (vacuum-melted electrolytic iron) was taken through A_3 in our dilatometer, it always decreased in length. To eliminate the effect of the slight compression present in our apparatus, a cylinder two inches long and three-eighths of an inch in diameter was placed on a bed of alundum in a vacuum furnace. The cylinder decreased in length permanently about 0.1 per cent each time it was taken through A_3. A rectangular piece of Wemco iron, treated in the same way, persistently extended itself at the edges and developed warts on its surfaces. Such experiments with large grained materials suggest that the dimensional changes observed are due to the relief of stresses set up by the transformation. The direction and magnitude of the changes may be determined by the temperature gradients and by the manner in which recrystallization takes place.

Samples 1 and 9 show in Fig. 2 transformation curves which differ definitely from those of the other eight samples. It may be pointed out that both of these samples as received contain relatively large amounts of oxygen, while the other samples had been treated to reduce the oxygen content.

HOWARD SCOTT[4] (presented the written discussion of Mr. Ziegler):

I acted as an intermediary in supplying samples for Mr. Austin and Mr. Ziegler, and perhaps both got the impression that our so called "Westinghouse iron" was supplied but that is not so. The analysis that Mr. Ziegler gives here is of the highest purity iron that has been produced in our laboratories. Mr. Austin's No. 3 sample was made up by another process which should give nearly the same purity, but its analysis has not been checked to the extent which Mr. Ziegler and Dr. Jensen have checked their iron.

Regarding the paper, there is very little to say, other than to praise it. There is only one exception that one might take, and that is to the recording of a single temperature for the transformation point in pure iron. It seems to me by so doing we are covering up a very important physical fact; namely, that the transformation on cooling is always observed at a lower temperature than on heating. What the significance of that is, I do not know, but the physicists will undoubtedly point it out some day.

Dr. Waterhouse spoke with surprise about finding the temperature 930 for A_3 in very pure iron. It may be even higher. In some early work done at the Bureau of Standards on iron carbon alloys an Ac_3 point around 900 degrees Cent. was obtained at low carbon contents. It dropped off suddenly when the carbon content exceeded 0.03 per cent. If you extrapolate the curve for higher carbon contents to zero, A_3 comes around 940 degrees Cent. The suggestion is that the lower the carbon content the higher the oxygen content. If oxygen lowers the transformation temperature and in the higher carbon contents there is no appreciable oxygen present such a shape of the curve may be expected.

Authors' Closure

The question of the purity of the "Westinghouse" iron brought up by Mr. Ziegler has been largely answered by Mr. Scott and need be considered but

[4]Westinghouse Electric and Manufacturing Co., Research Laboratories, East Pittsburgh.

briefly here. After our paper was in print we received, through the courtesy of Dr. F. R. Hensel, a sample of "Westinghouse" iron of the type referred to by Mr. Ziegler. Its composition was stated to be as follows: S 0.005, P 0.002, Mn 0.001, Si 0.003, O_2 0.001, C none; and it showed a very sharp transformation at 929 degrees Cent. on heating and at 928 degrees Cent. on cooling in agreement with the transformation temperature observed in other "pure" irons. Dr. Hensel stated that it had the highest magnetic permeability yet attained in the metals produced in his laboratory, which fact, together with the behavior in passing through the inversion, indicates that it is to be ranked with the purest of the specimens we examined.

Both Mr. McQuaid and Mr. Scott have mentioned the desirability of determining the effect of oxygen on the transformation temperature. We are entirely in agreement with them but the difficulty of obtaining suitable specimens has prevented us from making the determination up to the present.

Our remarks concerning the work of Harrington and Wood appear to have been interpreted as stronger criticism than we had intended that they be. If Dr. Harrington chooses to include in his definition of the second critical point the *a priori* statement that it shall not have any effect on the expansion but shall be observed only in thermal analysis there is, of course, nothing that we can say. He further implies, although he does not explicitly state, that the double effect is not found in pure iron; yet, the diagrams in his first paper (Harrington and Wood, TRANSACTIONS, American Society for Steel Treating, Vol. 18, 1933, p. 632) show the double transformation carried out to the pure iron axis.

The problem of the irreversible change in dimensions discussed by Dr. Walters appears to be a very complicated one as we have discovered in studying this effect in a number of pieces of iron of various shapes and sizes. We find with Dr. Walters that small "warts" are apt to appear on the surface and that extension occurs at the edges. Judging from our experiences the exact changes taking place depend on the nature and shape of the sample and on the temperature gradient existing in the metal at the time of transformation and cannot be accurately predicted. In this connection we have been informed in a personal communication from Dr. Esser at Aachen that careful X-ray studies in his laboratory indicate that the change in lattice parameter at the inversion is reversible within the limit of error of measurement.

We are indebted to Dr. Walters for calling our attention to an error in Fig. 2—No. 1. The curve starts at the left with the arrow pointing right and should cross the other curve and continue down along the curve with the arrow pointing to the upper left. The cooling curve, which has erroneously been given an arrow pointing down to the lower right, should cross the other curve and finish as shown in the figure.

In conclusion we should like to call attention to the paper of Esser and Müller (Archiv Eisenhüttenwesen, Vol. 7, 1933/34, p. 265) which appeared in the same month as our paper, giving the lattice constants of pure iron as a function of temperature. They found that the minimum in the coefficient curve at the magnetic inversion was even more pronounced than in our results for the macroscopic expansion.

BASIC OPEN-HEARTH CARBON STEEL FOR COLD HEADING—"INGOT TO WIRE"

By A. B. Arganbright

Abstract

In the manufacture of ingots the quality of the steel used is of prime importance and the better this material, the more care is needed in the making. An accurate record is kept of the temperature of the ingots during rolling and they are subjected to numerous tests in order to judge their suitability for cold heading. They are again carefully examined and the results noted before being prepared for wire drawing.

Certain standard specifications have been adopted by the manufacturers covering three types of wire and these are accurately followed. In the bundling room the wire is finally tested for grade as ordered, physical properties and surface imperfections. A complete history of the steel is then available, which includes definite information on the manufacture and rolling processes and all routine tests.

THIS paper deals with carbon steel made by the basic open-hearth process for use in cold heading products, ranging from 0.08 to 0.40 per cent carbon and 0.25 to 0.80 per cent manganese. The subject covers a broad field and far greater than can possibly be covered in this paper; nevertheless, before entering into the discussion of ingot making a word should be given on the subject of the quality of the steel.

The better the grade of steel to be produced, the greater becomes the need of more care and attention in its making. High grade steels have made the modern automobiles possible and the fact must not be overlooked that the many bolts and cold-headed parts which go to make up the automobile play just as an important role as any other piece of steel in its assembly. In the making of open-hearth carbon steel for cold-headed products, the raw materials are of prime importance both in the blast furnace and the open-hearth.

A paper presented before the Fifteenth Annual Convention of the society held in Detroit, October 2 to 6, 1933. The author, A. B. Arganbright, is superintendent of inspection and tests, Wheeling Steel Corporation, Portsmouth Works, Portsmouth, Ohio. Manuscript received June 29, 1933.

The hot metal or cold pig charged in the open-hearth must be within a specified analysis and accompanied by carefully selected scrap. Inasmuch as cleanliness is a prime requisite of cold heading steels, the refining and pouring operation along with proper adaption of the molds to the grade of steel, are of great importance. Rimmed, "effervescent," or killed steels are supplied depending upon carbon content or demand of the consumer.

Blooming Mill

An ingot evenly and thoroughly soaked is drawn from the soaking pits at approximately 2350 degrees Fahr., varying possibly a few degrees, depending upon carbon content, and enters the blooming mill approximately at 150 degrees lower than the drawing temperature due to loss of heat in travel. In the rolling, light drafts are beneficial, similar to forging which tends to eliminate rupture or cracking, which would later develop into seams. After the second draft, the ingot is turned and, thereafter, is turned every other draft until reduced to size for entering the continuous billet mill. The turning of the billet equalizes the work and reduces the collar marks, thereby minimizing the possibility of laps which would carry through to the finished billet.

An observer witnessing the rolling of ingots, records such information as temperature, number of drafts, and condition of surface. This report is passed on to the inspector at the billet mill and this report governs whether or not the ingot or melt is suitable for cold heading products.

Before entering the billet mill the bloom travels to a hydraulic shear and sufficient top and bottom discard taken to insure against piping and undue segregation. The amount of discard is governed mostly by grade of steel and type of mold used.

Continuous Billet Mill

The bloom enters the continuous mill at approximately 1850 degrees Fahr. and delivers at about the same temperature, in a 1¾ to 1⅞-inch billet which is sheared on a flying shear to the desired length for charging into the rod mill furnace.

During the rolling of the melt occasional crop ends are pickled to determine if there are any indications of laps, seams, or guide

scratches. The pickling tank is installed near the flying shears and this test enables the roller to have first hand information as to the quality of the product he is making.

Inspection and Testing of Billet on Hot Bed

After the melt has been rolled, the inspector carefully checks the observers' record of each ingot. Should any or all ingots show surface imperfections such as laps, cracks or scabs, this particular ingot or melt is not used for cold heading. Of the selected ingots a further inspection is given, such as the examination of ends for piping, surface inspection for laps, seams or scratches. The inspection for laps, seams or scratches, is further augmented by an upset test. This test comprises six or eight pieces about four inches long, cut from ends of billets, which are reheated and forged to about two inches. This definitely determines if there are any seams or laps present. The selected billets of the melt are then ready for rod rolling. From this point on, melts are kept separate and are labeled with tin tags showing the grade and the melt number.

Continuous Rod Mill

Billets are charged into a continuous furnace and delivered to the continuous rod mill at approximately 2100 degrees Fahr. and finished 100 to 200 degrees Fahr. above the upper critical point (Ac_3). This finishing temperature together with slow cooling produces grain growth, and the separation of ferrite and tends to reduce rolling strains. Slow cooling may be attained by individually covered conveyors which travel at each interval as a coil of rods is delivered from the mill. This structure resembles that of a normalized rod. The accompanying photomicrographs show the structure of a hot-rolled billet, hot-rolled rod, and of cold-drawn wire. By comparison it can be noted that the object is to endeavor to maintain the structure of the billet in the finished wire, except that a more rounded or equiaxed grain is preferable.

Inspection and Testing of Rods

The first inspection of the rod is at the finishing mill. A test is cut from a bundle before entering the covered conveyor and is inspected for gage and surface. This test is then given a 720-degree

twist while hot, for determining seams or laps. Testing at this point again enables the roller to know the quality of the product he is making. The final inspection of the rod is after the bundle leaves the covered conveyor. Here it is inspected for surface and gage; also subjected to a nick and break test for piping, seams and laps. The rods are then delivered to the cleaning house for the preparation of wire drawing.

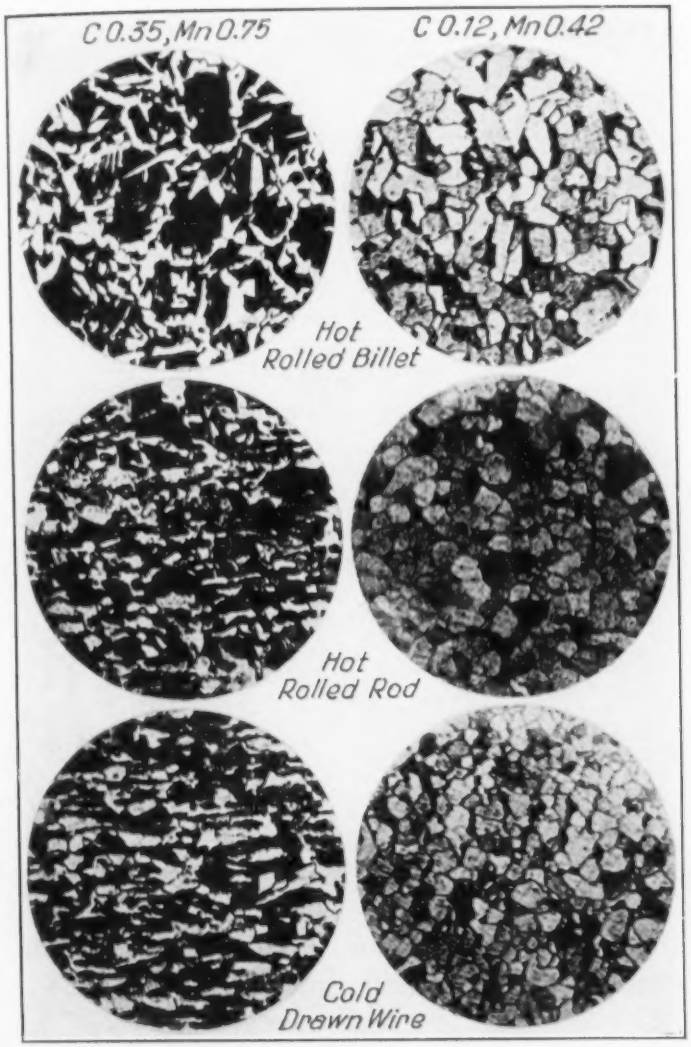
Cleaning House

The rods are given a still pickling in sulphuric acid, the percentage of acid and temperature depending upon the amount of scale. As brought out in the rod rolling, the finishing temperatures are very high which produces a heavy oxide, particularly so on some grades of steel. Therefore, the main factor is to get the rods pickled clean and as quickly as possible. After pickling they are water-rinsed to remove the acid, and sprayer with a high pressure hose to remove any particles of scale. They are then lime dipped which tends to neutralize any trace of acid and effect a coating which is necessary in wire drawing. The rods are then baked at 250 to 300 degrees Fahr. for approximately eight hours, which thoroughly dries the lime and gives an adhesive coating. Baking also will remove any hydrogen absorbed in pickling.

The coatings are also obtained in the cleaning house and are usually bright, light or heavy sull coated, and light or heavy sull coated with heavy lime. Bright wire after pickling is rinsed in clean water and immediately dipped in cold lime, while light and heavy sull coatings are attained by varying the time factor between the rinse and lime tub. Heavy limed wire is obtained by dipping in a hot lime tub.

Wire Drawing (Dry)

The majority of cold heading wire, cold drawn one hole from the rod, is drafted approximately thirty-five one-thousandths. It is then drawn through tungsten carbide dies to a single driven twenty-six block running approximately forty-five revolutions per minute. The tungsten carbide dies produce a very smooth wire accurate to gage, and while the initial cost is great, these dies are conducive to long life and low cost maintenance. The lubricant used is either grease or soap, depending upon finish desired by the consumer. In most instances grease-drawn wire is furnished.



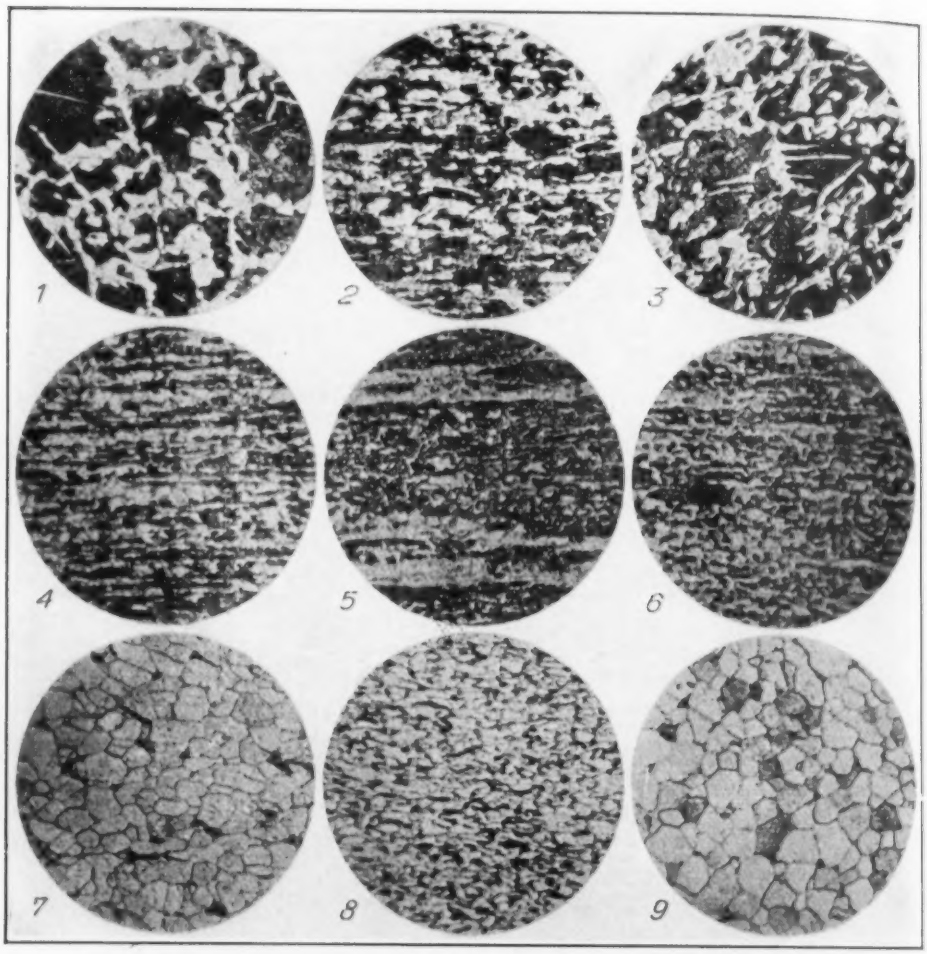
Photomicrographs of Basic Open-Hearth Carbon Steel. Billet to Wire.

Types of Wire for Cold Heading

Manufacturers' Standard Specifications adopted by the Association of American Steel Manufacturers, Technical Committee, 1933, gives three types of wire:

(1) Annealed, or annealed, cleaned and lime coated—when maximum softness and ductility are required, and a bright surface is not essential.

(2) Bright processed—when maximum softness and ductility with a bright smooth surface are required. Wire so processed is



Photomicrographs of Carbon Steel Wire for Cold Heading

Fig. 1—0.33 Per Cent Carbon from Normalized Rod.
Fig. 2—0.35 Per Cent Carbon from Pot Annealed Rod.
Fig. 3—0.35 Per Cent Carbon from Hot-Rolled Rod Finished Above Upper Critical and Slowly Cooled.
Fig. 4—0.36 Per Cent Carbon from Hot-Rolled Rod Finished Below Upper Critical.
Figs. 5 and 6—0.16 Per Cent Carbon Screw Stock. Sulphur Segregation.
Fig. 7—0.12 Per Cent Carbon from Hot-Rolled Rod Finished Above Upper Critical and Slowly Cooled.
Fig. 8—Same as Fig. 7 But Finished Below Upper Critical.
Fig. 9—0.06 Per Cent Carbon Hot-Rolled Rod Finished Above Upper Critical and Slowly Cooled.

necessary for severe cold heading operations; where the diameter of the head is 2½ times greater than the diameter of the wire—where the head is very thin—or where there are sharp corners to fill out under the head.

(3) Bright—when only moderate cold heading or cold forming is done.

Manufacturers' Standard Specifications also mention that grades

30 and 35, "25 to 40 carbon," should be ordered drawn from normalized rods to insure the necessary uniformity and plasticity for cold heading.

Final Tests and Inspection

The wire is delivered to the bundling room for final tests, inspection, and bundling in the order following: The wire is first checked for grade as ordered. Series of tests are then cut for the determination of chemical and physical properties; the physical properties are based on one hole wire as being approximately 20,000 pounds per square inch higher in ultimate strength than the rod from which the wire was drawn.

Wire is given surface inspection for finish, scratches or slivers, and micrometer reading for gage as ordered, with permissible variation of plus or minus two one-thousandths.

Tests are then cut from both the front and back end of each coil, of which one half of each is given a nick and break test for piping. The other half of each piece is given a twist test of 360 degrees and back, to determine seams or laps. As a further safeguard at the time this inspection is being carried on, several pieces throughout the melt are cut about four inches long, immersed in a 50 per cent solution of hydrochloric acid for ten minutes, at approximately 170 degrees Fahr., for determining the general surface condition. Frequently pieces are sawed from these tests and forged cold in order to predict the results of processing in consumer's plant.

After the final inspection there is available a complete history of the steel involved. This includes comprehensive data relative to the manufacture and rolling processes, along with the numerous routine tests previously outlined.

In conclusion it may be stated that along with advanced steel making, metallurgical control plus ways and means of testing, play an important part in the steel industry. Close co-operation between the consumer and manufacturer as to the articles to be upset and the method of upset, enables the inspection department to better carry on its duties and deliver a satisfactory product.

DISCUSSION

Written Discussion: By C. L. Harvey, The Lamson and Sessions Co., Kent, Ohio.

I take this opportunity to congratulate Mr. Arganbright on his paper,

which so clearly explains the care required to produce wire rods and drawn wire of a grade suitable for cold heading. It is, indeed, gratifying to know that the producers of these steels realize the importance of uniform, sound material and that they are making such efforts to produce it.

It has been my experience, that as a general rule, the mills are producing rod and wire of satisfactory quality as regards composition and the absence of internal defects. However, there is still considerable room for improvement with respect to surface conditions and to wire coatings.

In the cold upsetting operation, the external portion of the upset is put in tension and any defects, particularly longitudinal defects, such as scratches or seams, have a notch effect and are greatly exaggerated in the upsetting process. This is especially true of the higher carbon steels, which work-harden rapidly. While the percentage of wire showing these surface defects is small as compared to the total tonnage of wire used, it is of considerable concern to the manufacturer. If the defects are of such a character that the entire coil of rod or wire is affected, it is a relatively simple matter to inspect the material by means of a twist test or by an acid etch test. However, if the defects are local, such tests may not be positive and it becomes necessary to give the finished product a 100 per cent inspection. This is both slow and expensive.

Another point which I believe is worthy of emphasis is that of wire coatings. The use of sintered carbide drawing dies has improved the quality of wire finishes tremendously, but there is still considerable development work to be done on the types of coatings. The steel itself may be perfectly sound internally and externally, but unless the coating applied in the wire drawing operation is uniform and of the right type, the finished wire may be absolutely worthless from the manufacturer's standpoint. This is especially true of the wire used in the solid-die extrusion process.

Aside from the points mentioned, which concern the production of physically sound wire and wire rods, there remains a tremendous amount of basic work to be done on the "headability" of steels. Frequently the manufacturer of cold-headed products finds heats of steel of apparently the same grade, which perform differently. Until the causes of such variation can be determined, the mills cannot have full control of their product. Quantitative measures of "headability" must be determined, standard methods of testing adopted, and then the effects of dissolved gases, oxides, etc., studied before these differences in behavior are understood and placed under control.

It is to be hoped that by close co-operation between producer and consumer such basic work will be done and our knowledge of the factors affecting the cold working of metals increased.

E. J. P. FISHER:[1] I would like to ask Mr. Arganbright if he finds the twist test on the rod as satisfactory a gage of cold heading properties as a drop test or cold heading test.

A. B. ARGANBRIGHT: We have found that the twist test is a far better test, particularly so on the rod. With the upset test we have at times been unable to determine the direct cause of the defect or the difference between seams and scratches, as they both open up by this test. Furthermore, that the

[1]Physical metallurgist, Keystone Steel and Wire Company, Peoria, Ill.

rod which is tested hot gives a chance to determine any trouble right then rather than wait until the material is cool, as it takes about forty minutes to go through the conveyor.

E. M. SLAUGHTER:[2] I would like to ask the speaker what work has been done to determine the preference for types of wire for cold heading. In the paper normalized wire has been mentioned. Quite a lot of spheroidized material in the higher carbon or rather medium carbon over 0.30 per cent has been used, and there is some question in my mind as to the preferred type of rod to use for cold heading. I wonder if any work has been done to determine the type of structure best suited in this particular grade of medium straight carbon wire.

A. B. ARGANBRIGHT: With reference to the first question as to the grade, the grade is specified by the buyer. Did you mean an S.A.E. 1050 or 1035?

E. M. SLAUGHTER: S.A.E. 1035.

A. B. ARGANBRIGHT: Our experience is that a normalized structure is far better suited for upsetting. If the grain is very fine, an amorphous structure is likely to develop in the upset. Therefore the reason for a large grain as shown in the preprint. The best way to get this grain in S.A.E. 1035 is to normalize.

J. L. MCCLOUD:[3] As I understand the question, do you find that the majority of buyers prefer normalized wire in the higher carbon grades, and is it your belief that only normalized wire should be used?

A. B. ARGANBRIGHT: That is a very difficult question to answer. There are some concerns that will not use anything else but normalized wire in the S.A.E. 1035, and other concerns that use hard drawn wire. The American Association of Steel Manufacturers recommends grades S.A.E. 1030 and 1035 wire drawn from normalized rods. If this structure can be obtained without normalizing, all right.

E. M. SLAUGHTER: Frankly I am not fully satisfied yet. Some tests have been made showing more ductility in spheroidized wire than normalized wire. In a normalized wire there are patches of ferrite which might assist in the cold forming operations. Of the two types of wire we have personal ideas which may perform most satisfactorily, but what I am interested in is whether or not there is any concrete evidence that can be shown giving preference to either of these two types.

A. B. ARGANBRIGHT: If you put the question that way, I cannot answer it. We furnish hard drawn wire to do upsetting and it is up to the buyer to let us know his requirements. We do not furnish spheroidized wire.

J. L. MCCLOUD: I think that is summed up in the last sentence of Mr. Arganbright's paper. As I understand Mr. Arganbright, no broad statements can be made in comparison of the proper choice of material.

R. E. CHRISTIN:[4] May I ask the author if he aims to furnish all rimmed steel in his cold heading wire, and why?

A. B. ARGANBRIGHT: Again, we are in the steel business and furnish wire

[2]Metallurgist, The National Acme Company, Cleveland.

[3]Metallurgical department, Ford Motor Company, Dearborn, Mich.

[4]Metallurgist, Columbus Bolt Works, Columbus, Ohio.

as specified by the customer. If you ask me what we like to furnish I will tell you. In the lower carbon we prefer furnishing the rimmed steel for the reason of better upsetting quality and fewer seams.

In answer to the remarks of Mr. Harvey may I again say that this paper covers mostly what you might call a physical inspection from the ingot through the various processing to the finished wire. It of course takes in surface, seams, scratches, and coatings. These must be very uniform and of a nature to suit the customer.

In regard to the percentage of elongation or ductility as affected by factors going back beyond the ingot to the open-hearth, may I say that we also take the same precautions and the same inspection measures as we do from the ingot to the wire.

E. J. P. FISHER: It seems to me that there has been a definite call here for a discussion of microstructures as compared to cold heading properties. There must be some consumers here who have made such a study. I know of at least one who has, but I don't know whether he is in the room.

A. B. ARGANBRIGHT: If you will turn to page 475 in the preprint, you will see some micrographs. These may be all wrong but we tried to furnish structures suitable for upsetting. You will notice there, the grain size and particularly the shape of grains, showing absence of rolling strains. That is the point brought up as to finishing above the recalescent point followed by slow cooling. In the hot-rolled rod there is shown both S.A.E. 1035 and the lower carbon, S.A.E. 1015, also the cold drawn wire shown underneath. We have found such a structure to work satisfactorily.

E. J. P. FISHER: The other point was with regard to a comparison between a "process" annealed wire and a "normalized" wire; i.e., a wire annealed below the critical range and one heated above the critical range and cooled out of the furnace slowly.

A. B. ARGANBRIGHT: There is not a whole lot of difference between the physical characteristics and structure of process annealed and normalized. The term "normalized" is really a misnomer. Would say on general practice the S.A.E. 1035 would be specified normalized, whereas on lower carbons S.A.E. 1015 or 1020 for severe upset jobs would specify process annealed.